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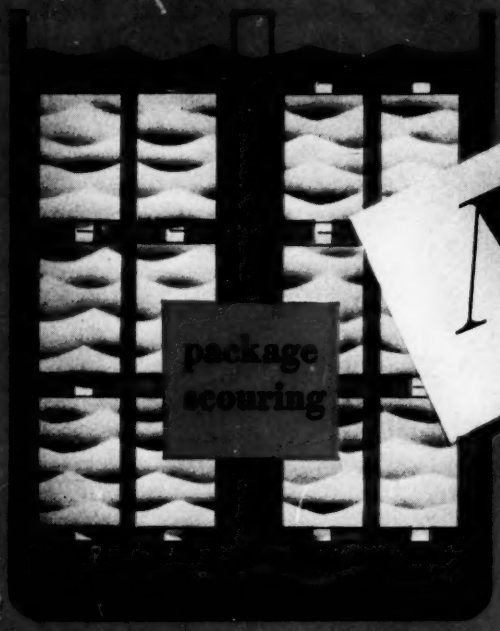

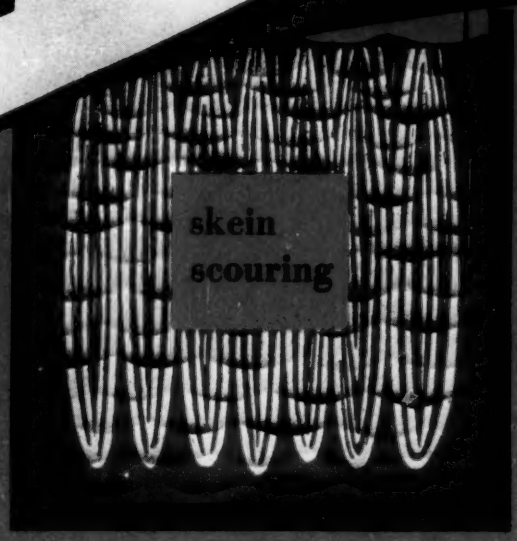

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A SIMPLE SOLUTION TO THE "ARTIFICIAL LIGHT" PROBLEM

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INTRODUCTION

ONE of the most difficult problems faced by an experienced colorist is that of matching a given sample for all conditions of illumination. Choice of dyestuffs to be used in matching a sample in daylight alone or tungsten light alone is usually a very simple matter. Choice of the proper dyestuffs to make a match for both illuminants, however, is often a very difficult job unless instrumental means are used. The colorist's usual procedure is to note how the sample changes in artificial light and then to try to use components which change in the same manner. If, for example, the sample shows little change in hue as the illuminant is changed, the colorist will try to use a component which shows little change, or else he will try to choose components which change hue in opposite directions in order that their hue changes might cancel one another. Often a very large number of different combinations of dyestuffs must be tried before a suitable match can be made.

The basis of the difficulty of color matching for different illuminants lies in the eye's inability to analyze a color, or to break it down into its component parts. Although the trained ear can detect the several notes making up a musical chord, even the most highly trained eye cannot detect the relative amounts of differently-colored light reflected from a dyed cloth. The eye perceives only an overall impression of a color, which might be produced by many different combinations of colored light reflected from the sample. This state of affairs leads to the condition in which a sample may match a standard in daylight but not in tungsten light. Consider, for example, the two spectrophotometric curves of Figure 1. These curves represent the percentage of colored light reflected from two colored samples. Both samples, one represented by the solid line, the other

H R Davidson

by the dashed line, are yellowish browns and are fairly close matches in daylight. The curves indicate that the samples reflect little of the blue light, but reflect progressively more light in the green, yellow, orange and red portions of the spectrum. The exact percentages reflected by each sample at each wavelength of light are quite different even though the eye sees relatively little color difference between them under daylight illumination. Now, however, if the illuminant is changed from daylight to tungsten light, one of the samples goes green, the other goes red, and the eye sees a much larger difference between them.

The solution to this problem of making a match for all conditions of illumination is, in principle, very simple. If the spectrophotometric curves of the two colors are identical, the colors will match under all types of illumination. In other words, it is unnecessary to consider explicitly the manner of change in artificial light of either the standard or the dye components to be used in making the match. As far as color goes, it is only necessary to choose components so that the spectrophotometric curves of the standard can be matched. Furthermore, simple calculations can be made to determine the amount of each component needed to make the match, although usually it will be found most efficient to make approximate calculations and allow the experienced colorists to make the final formulation by eye.

These facts are well known to many colorists and dyers, but often the spectrophotometric method is not employed simply because of a mistaken belief that it is slow and complicated. The purpose of this paper is to show by means of a practical example that the spectrophotometric method is neither slow nor complicated, and that it can be a very valuable tool in the hands of a trained colorist. Nothing contained herein is to be considered new, either in the sense of being original or untried, but it is hoped that a detailed example will promote more general use of the method.

The following description of the spectrophotometric method of solving the artificial light problem will, at first glance, appear complicated and long-winded. Note, however, that the total time required for this particularly complex problem was less than two hours for choice of the components and making the initial trial calculations, and about twenty minutes for making each of the two correction calculations. Much less time would be required for a less complex problem. Only two trial dyeings were required.

Once the method itself is understood, the details described below will appear obvious rather than complicated.

CHOICE OF COMPONENTS

The spectrophotometric curve of a wool flannel dyeing of the dyestuff we wish to match is shown by the solid line in Figure 1. Because of certain undesirable properties of this dyestuff for a particular application, we wish to substitute a mixture of dyestuffs so chosen as to provide a match in both daylight and artificial light.

The first step in choosing the proper components is to note that the curve of the dyeing to be matched, which we will call "the standard" from here on, indicates considerable absorption of light in the blue or short wavelength end of the spectrum, with decreasing absorption, or increasing reflectance, at longer wavelengths. A yellow dye is evidently needed to give the

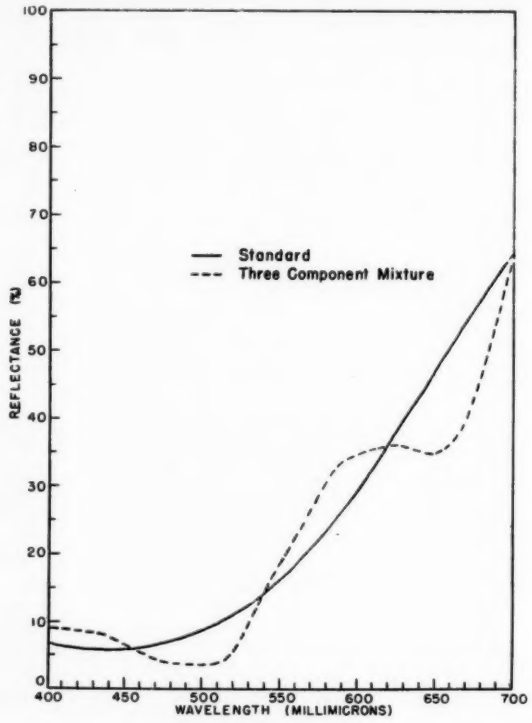

Figure 1
Three Component Mixture

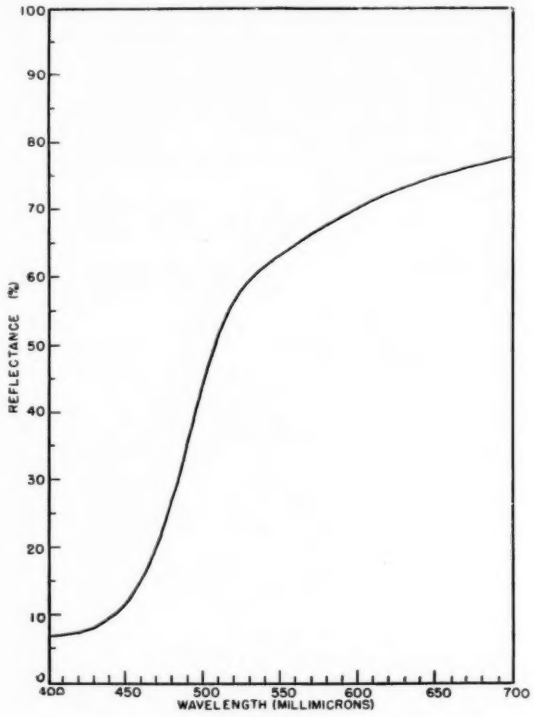

Figure 2
0.25% Fast Light Yellow GGXN Conc

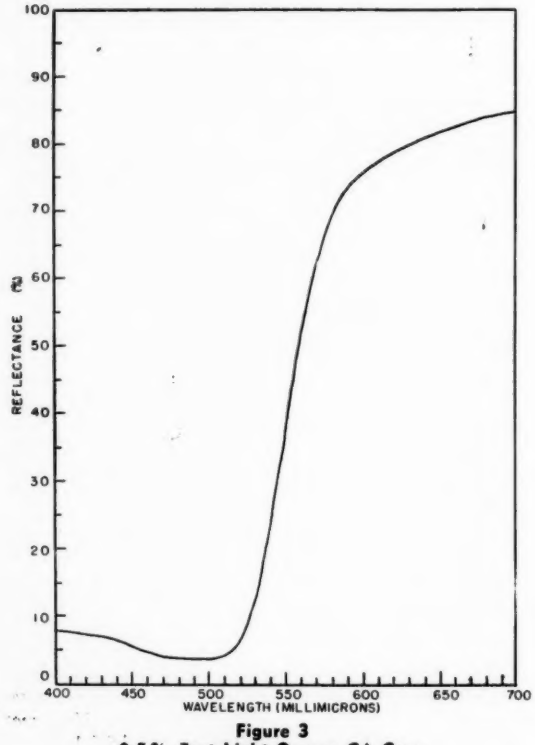

Figure 3
0.5% Fast Light Orange GA Conc

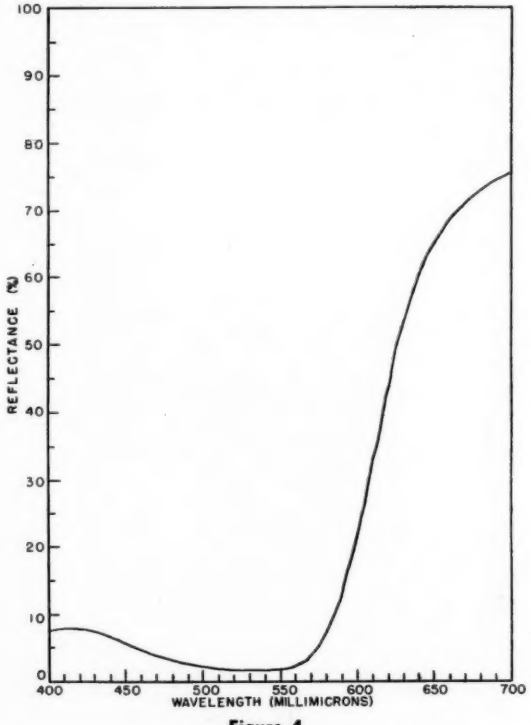

Figure 4
2% Fast Light Red BA

required absorption in the blue region, possibly Fast Light Yellow GGXN, a spectrophotometric curve of which is shown in Figure 2. Note that this yellow reflects too much light at wavelengths longer than 470 mμ (millimicrons). This means that we need an orange, such as Fast Light Orange GA, the curve of which is shown in Figure 3. When mixed to-

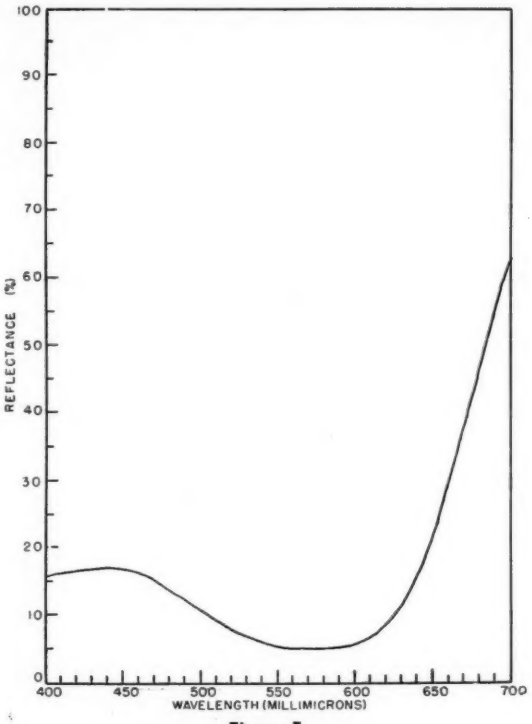

Figure 5
0.5% Victoria Fast Violet RRN Ex

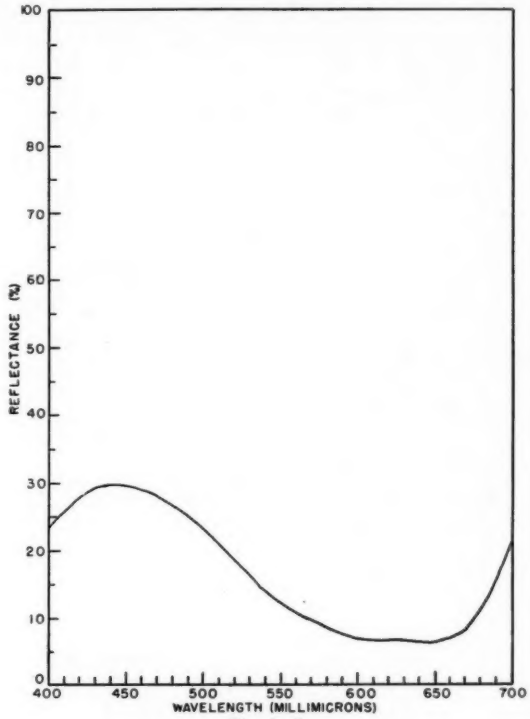

Figure 6
0.5% Alizarine Blue SAP

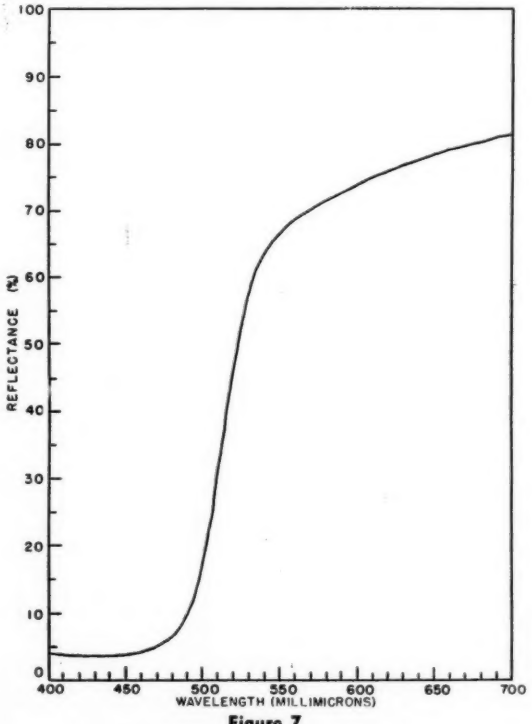

Figure 7
0.5% Tartrazine C Ex

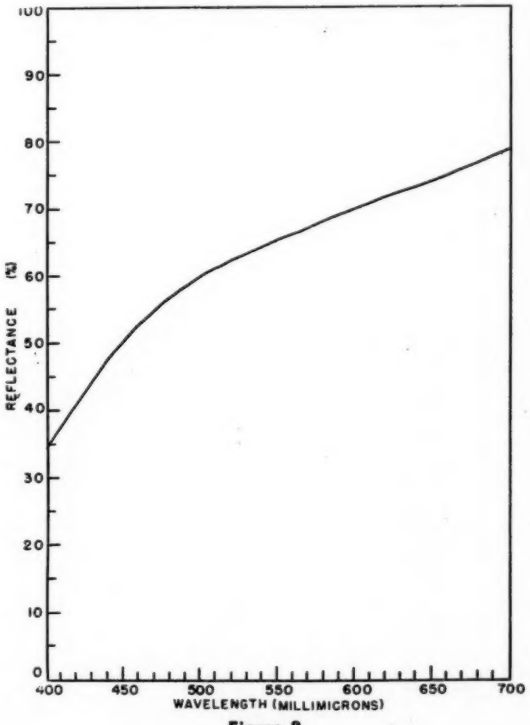

Figure 8
Undyed Wool

gether, the yellow and orange should approximate the shape of the solid curve in Figure 1 from 400 mμ to about 530 mμ, but the mixture will reflect too much light at longer wavelengths. We therefore need a red. Fast Light Red BA will be suitable, and its curve is given in Figure 4. Next a violet will be needed to absorb light in the neighborhood of 580 mμ, and finally a blue to absorb in the neighborhood of 640 mμ. We would also like to use a dye which absorbs in the neighborhood of 690 mμ, but no suitable ones are available. We may use Victoria Fast Violet RRN Conc for the violet, and Alizarine Blue SAP for the blue. The curves for these dyes are given in Figures 5 and 6 respectively.

Any colorist who owns, or has access to, a spectrophotometer should have a file of spectrophotometric curves of standard dyestuffs. The curves in Figures 2 to 8 should be part of that file. When such a collection of curves is available, only a few minutes work are required to leaf through it and pick out the curves of the dyestuffs most suitable for matching the standard. Of course, various fastness and application properties of the dyestuffs must be considered in making a final choice of components, but as far as color alone goes, the choice may be based solely on the file of spectrophotometric curves. Note that all of the curves used here are of dyeings rather than solutions of the dyestuffs. For best results, of course, the spectrophotometric curves should be available for the dyestuffs applied to the particular type of textile on which the standard to be matched has been dyed.

METHOD OF CALCULATING THE DYEBATH FORMULA

After the appropriate components have been chosen, the amount of each required may be calculated by use of the following formula:

F is a simplified notation, an abbreviation for the fraction K/S, or the quantity $(1-R)^2/2R$ where R is the reflectance of the cloth at a specified wavelength *(1)*. Values of F as a function of R are given in Table I.* Subscripts 1, 2, 3, . . . designate dye 1, dye 2, etc, subscript o designates the undyed material, and A, B, C, . . . denote the concentrations for which the spectrophotometric curves of dyes 1, 2, 3, were obtained. a, b, c, . . . denote the concentrations of dyes 1, 2, 3, . . ., respectively, used in the mixture. The last term of the equation is a correction factor to allow for the color of the undyed material. Except for pastel shades, this term is usually close to zero and can be neglected. By use of equa-

* This table of mathematical values appeared in *Technical Bulletin* 2 (E I du Pont de Nemours & Co, Inc), No 1, April (1946).

$$F_M = \frac{a}{A} F_1 + \frac{b}{B} F_2 + \frac{c}{C} F_3 + \ldots F_o \left(1 - \frac{a}{A} - \frac{b}{B} - \frac{c}{C} \ldots\right) \quad (1)$$

TABLE I
VALUES OF "F" AS A FUNCTION OF "R"

R	F	R	F	R	F	R	F	R	F	R	F
0.0		.7	7.800	.4	3.443	17.0	2.026	.7	1.316	.4	.903
.1	449.000	.8	7.650	.5	3.405	.1	2.009	.8	1.307	.5	.897
.2	249.001	.9	7.513	.6	3.368	.2	1.993	.9	1.298	.6	.891
.3	165.668	6.0	7.563	.7	3.332	.3	1.977	23.0	1.289	.7	.886
.4	124.002	.1	7.227	.8	3.296	.4	1.961	.1	1.280	.8	.880
.5	99.002	.2	7.096	.9	3.261	.5	1.945	.2	1.271	.9	.875
.6	82.336	.3	6.968	12.0	3.227	.6	1.929	.3	1.262	29.0	.869
.7	70.432	.4	6.844	.1	3.193	.7	1.913	.4	1.254	.1	.864
.8	61.504	.5	6.725	.2	3.159	.8	1.898	.5	1.245	.2	.858
.9	54.561	.6	6.609	.3	3.127	.9	1.883	.6	1.237	.3	.853
1.0	49.005	.7	6.496	.4	3.094	18.0	1.868	.7	1.228	.4	.848
.1	44.460	.8	6.387	.5	3.062	.1	1.853	.8	1.220	.5	.842
.2	40.673	.9	6.281	.6	3.031	.2	1.838	.9	1.212	.6	.837
.3	37.468	7.0	6.178	.7	3.001	.3	1.824	24.0	1.203	.7	.832
.4	34.720	.1	6.078	.8	2.970	.4	1.809	.1	1.195	.8	.827
.5	32.341	.2	5.980	.9	2.940	.5	1.795	.2	1.187	.9	.822
.6	30.258	.3	5.886	13.0	2.911	.6	1.781	.3	1.179	30.0	.817
.7	28.420	.4	5.794	.1	2.882	.7	1.767	.4	1.171	.1	.812
.8	26.787	.5	5.704	.2	2.854	.8	1.754	.5	1.163	.2	.807
.9	25.325	.6	5.617	.3	2.826	.9	1.740	.6	1.156	.3	.802
2.0	24.010	.7	5.532	.4	2.798	19.0	1.727	.7	1.148	.4	.797
.1	22.820	.8	5.449	.5	2.771	.1	1.713	.8	1.140	.5	.792
.2	21.738	.9	5.369	.6	2.744	.2	1.700	.9	1.133	.6	.787
.3	20.751	8.0	5.290	.7	2.718	.3	1.687	25.0	1.125	.7	.782
.4	19.845	.1	5.213	.8	2.692	.4	1.674	.1	1.118	.8	.777
.5	19.012	.2	5.139	.9	2.667	.5	1.662	.2	1.110	.9	.773
.6	18.244	.3	5.066	14.0	2.641	.6	1.649	.3	1.103	31.0	.768
.7	17.532	.4	4.994	.1	2.617	.7	1.637	.4	1.095	.1	.763
.8	16.871	.5	4.925	.2	2.592	.8	1.624	.5	1.088	.2	.759
.9	16.256	.6	4.857	.3	2.568	.9	1.612	.6	1.081	.3	.754
3.0	15.682	.7	4.791	.4	2.544	20.0	1.600	.7	1.074	.4	.749
.1	15.145	.8	4.726	.5	2.521	.1	1.588	.8	1.067	.5	.745
.2	14.641	.9	4.662	.6	2.498	.2	1.576	.9	1.060	.6	.740
.3	14.168	9.0	4.601	.7	2.475	.3	1.565	26.0	1.053	.7	.736
.4	13.723	.1	4.540	.8	2.452	.4	1.553	.1	1.046	.8	.731
.5	13.303	.2	4.481	.9	2.430	.5	1.542	.2	1.039	.9	.727
.6	12.907	.3	4.423	15.0	2.408	.6	1.530	.3	1.033	32.0	.722
.7	12.532	.4	4.366	.1	2.387	.7	1.519	.4	1.026	.1	.718
.8	12.177	.5	4.311	.2	2.365	.8	1.508	.5	1.019	.2	.714
.9	11.840	.6	4.256	.3	2.344	.9	1.497	.6	1.013	.3	.709
4.0	11.520	.7	4.203	.4	2.324	21.0	1.486	.7	1.006	.4	.705
.1	11.216	.8	4.151	.5	2.303	.1	1.475	.8	.997	.5	.701
.2	10.926	.9	4.100	.6	2.283	.2	1.464	.9	.993	.6	.697
.3	10.649	10.0	4.050	.7	2.263	.3	1.454	27.0	.987	.7	.693
.4	10.386	.1	4.001	.8	2.244	.4	1.443	.1	.981	.8	.688
.5	10.134	.2	3.953	.9	2.224	.5	1.433	.2	.974	.9	.684
.6	9.893	.3	3.906	16.0	2.205	.6	1.423	.3	.968	33.0	.680
.7	9.662	.4	3.860	.1	2.186	.7	1.413	.4	.962	.1	.676
.8	9.441	.5	3.814	.2	2.167	.8	1.403	.5	.956	.2	.672
.9	9.229	.6	3.770	.3	2.149	.9	1.393	.6	.950	.3	.668
5.0	9.025	.7	3.718	.4	2.131	22.0	1.383	.7	.944	.4	.664
.1	8.829	.8	3.684	.5	2.113	.1	1.373	.8	.938	.5	.660
.2	8.641	.9	3.642	.6	2.095	.2	1.363	.9	.932	.6	.656
.3	8.460	11.0	3.600	.7	2.078	.3	1.354	28.0	.926	.7	.652
.4	8.286	.1	3.560	.8	2.060	.4	1.344	.1	.920	.8	.648
.5	8.118	.2	3.520	.9	2.043	.5	1.335	.2	.914	.9	.644
.6	7.957	.3	3.481			.6	1.325	.3	.908		

TABLE I (Concluded)

R	F	R	F	R	F	R	F	R	F	R	F
34.0	.641	45.0	.336	56.0	.173	67.0	.08127	78.0	.03103	89.0	.00680
.1	.637	.1	.334	.1	.172	.1	.08066	.1	.03070	.1	.00667
.2	.633	.2	.332	.2	.171	.2	.08005	.2	.03039	.2	.00654
.3	.629	.3	.330	.3	.170	.3	.07944	.3	.03007	.3	.00641
.4	.625	.4	.328	.4	.169	.4	.07884	.4	.02976	.4	.00628
.5	.622	.5	.326	.5	.167	.5	.07824	.5	.02944	.5	.00616
.6	.618	.6	.324	.6	.166	.6	.07764	.6	.02913	.6	.00604
.7	.614	.7	.323	.7	.165	.7	.07705	.7	.02882	.7	.00591
.8	.611	.8	.321	.8	.164	.8	.07646	.8	.02852	.8	.00579
.9	.607	.9	.319	.9	.163	.9	.07588	.9	.02821	.9	.00567
35.0	.604	46.0	.317	57.0	.162	68.0	.07529	79.0	.02791	90.0	.00555
.1	.600	.1	.315	.1	.161	.1	.07471	.1	.02761	.1	.00544
.2	.596	.2	.313	.2	.160	.2	.07414	.2	.02731	.2	.00532
.3	.593	.3	.311	.3	.159	.3	.07356	.3	.02702	.3	.00521
.4	.589	.4	.310	.4	.158	.4	.07299	.4	.02672	.4	.00510
.5	.586	.5	.308	.5	.157	.5	.07243	.5	.02643	.5	.00499
.6	.582	.6	.306	.6	.156	.6	.07186	.6	.02614	.6	.00488
.7	.579	.7	.304	.7	.155	.7	.07130	.7	.02585	.7	.00477
.8	.576	.8	.302	.8	.154	.8	.07074	.8	.02557	.8	.00466
.9	.572	.9	.301	.9	.153	.9	.07019	.9	.02528	.9	.00456
36.0	.569	47.0	.299	58.0	.152	69.0	.06964	80.0	.02500	91.0	.00445
.1	.566	.1	.297	.1	.151	.1	.06909	.1	.02472	.1	.00435
.2	.562	.2	.295	.2	.150	.2	.06854	.2	.02444	.2	.00425
.3	.559	.3	.294	.3	.149	.3	.06800	.3	.02417	.3	.00415
.4	.556	.4	.292	.4	.148	.4	.06746	.4	.02389	.4	.00405
.5	.552	.5	.290	.5	.147	.5	.06692	.5	.02362	.5	.00395
.6	.549	.6	.288	.6	.146	.6	.06639	.6	.02335	.6	.00385
.7	.546	.7	.287	.7	.145	.7	.06586	.7	.02308	.7	.00376
.8	.543	.8	.285	.8	.144	.8	.06533	.8	.02281	.8	.00366
.9	.540	.9	.283	.9	.143	.9	.0648	.9	.02255	.9	.00357
37.0	.536	48.0	.282	59.0	.142	70.0	.06429	81.0	.02228	92.0	.00348
.1	.533	.1	.280	.1	.142	.1	.06377	.1	.02202	.1	.00339
.2	.530	.2	.278	.2	.141	.2	.06325	.2	.02176	.2	.00330
.3	.527	.3	.277	.3	.13967	.3	.06274	.3	.02151	.3	.00321
.4	.524	.4	.275	.4	.13875	.4	.06223	.4	.02125	.4	.00313
.5	.521	.5	.273	.5	.13784	.5	.06172	.5	.02100	.5	.00304
.6	.518	.6	.272	.6	.13693	.6	.06122	.6	.02075	.6	.00296
.7	.515	.7	.270	.7	.13602	.7	.06071	.7	.02050	.7	.00287
.8	.512	.8	.269	.8	.13512	.8	.06021	.8	.02025	.8	.00279
.9	.509	.9	.267	.9	.13422	.9	.05972	.9	.02000	.9	.00271
38.0	.506	49.0	.265	60.0	.13333	71.0	.05923	82.0	.01976	93.0	.00263
.1	.503	.1	.264	.1	.13245	.1	.05873	.1	.01951	.1	.00256
.2	.500	.2	.262	.2	.13156	.2	.05825	.2	.01927	.2	.00248
.3	.497	.3	.261	.3	.13069	.3	.05776	.3	.01903	.3	.00241
.4	.494	.4	.259	.4	.12981	.4	.05728	.4	.01880	.4	.00233
.5	.491	.5	.258	.5	.12895	.5	.05680	.5	.01856	.5	.00226
.6	.488	.6	.256	.6	.12808	.6	.05632	.6	.01833	.6	.00219
.7	.485	.7	.255	.7	.12722	.7	.05585	.7	.01809	.7	.00212
.8	.483	.8	.253	.8	.12637	.8	.05538	.8	.01786	.8	.00205
.9	.480	.9	.251	.9	.12552	.9	.05491	.9	.01764	.9	.00198
39.0	.477	50.0	.250	61.0	.12467	72.0	.05444	83.0	.01741	94.0	.00191
.1	.474	.1	.248	.1	.12383	.1	.05398	.1	.01718	.1	.00185
.2	.472	.2	.247	.2	.12299	.2	.05352	.2	.01696	.2	.00179
.3	.469	.3	.246	.3	.12216	.3	.05306	.3	.01674	.3	.00172
.4	.466	.4	.244	.4	.12133	.4	.05261	.4	.01652	.4	.00166
.5	.463	.5	.243	.5	.12051	.5	.05216	.5	.01630	.5	.00160
.6	.461	.6	.241	.6	.11969	.6	.05171	.6	.01609	.6	.00154
.7	.458	.7	.240	.7	.11887	.7	.05126	.7	.01587	.7	.00148
.8	.455	.8	.238	.8	.11806	.8	.05081	.8	.01566	.8	.00143
.9	.453	.9	.237	.9	.11725	.9	.05037	.9	.01545	.9	.00137
40.0	.450	51.0	.235	62.0	.11645	73.0	.04993	84.0	.01524	95.0	.00132
.1	.447	.1	.234	.1	.11565	.1	.04949	.1	.01503	.1	.00126
.2	.445	.2	.233	.2	.11486	.2	.04906	.2	.01482	.2	.00121
.3	.442	.3	.231	.3	.11407	.3	.04863	.3	.01462	.3	.00116
.4	.440	.4	.230	.4	.11328	.4	.04820	.4	.01442	.4	.00111
.5	.437	.5	.228	.5	.11250	.5	.04777	.5	.01422	.5	.00106
.6	.435	.6	.227	.6	.11172	.6	.04735	.6	.01402	.6	.00101
.7	.432	.7	.226	.7	.11095	.7	.04693	.7	.01382	.7	.00097
.8	.429	.8	.224	.8	.11018	.8	.04651	.8	.01362	.8	.00092
.9	.427	.9	.223	.9	.10941	.9	.04609	.9	.01343	.9	.00088
41.0	.425	52.0	.222	63.0	.10865	74.0	.04568	85.0	.01324	96.0	.00083
.1	.422	.1	.220	.1	.10789	.1	.04526	.1	.01304	.1	.00079
.2	.420	.2	.219	.2	.10714	.2	.04485	.2	.01285	.2	.00075
.3	.417	.3	.218	.3	.10639	.3	.04445	.3	.01267	.3	.00071
.4	.415	.4	.216	.4	.10564	.4	.04404	.4	.01248	.4	.00067
.5	.412	.5	.215	.5	.10490	.5	.04364	.5	.01230	.5	.00063
.6	.410	.6	.214	.6	.10416	.6	.04324	.6	.01211	.6	.00060
.7	.408	.7	.212	.7	.10343	.7	.04284	.7	.01193	.7	.00056
.8	.405	.8	.211	.8	.10270	.8	.04245	.8	.01175	.8	.00053
.9	.403	.9	.210	.9	.10197	.9	.04206	.9	.01157	.9	.00050
42.0	.400	53.0	.208	64.0	.10125	75.0	.04167	86.0	.01140	97.0	.00046
.1	.398	.1	.207	.1	.10053	.1	.04128	.1	.01122	.1	.00043
.2	.396	.2	.206	.2	.09982	.2	.04089	.2	.01105	.2	.00040
.3	.394	.3	.205	.3	.09910	.3	.04051	.3	.01087	.3	.00037
.4	.391	.4	.203	.4	.09840	.4	.04013	.4	.01070	.4	.00035
.5	.389	.5	.202	.5	.09769	.5	.03975	.5	.01054	.5	.00032
.6	.387	.6	.201	.6	.09699	.6	.03938	.6	.01036	.6	.00030
.7	.384	.7	.200	.7	.09630	.7	.03900	.7	.01020	.7	.00027
.8	.382	.8	.198	.8	.09560	.8	.03863	.8	.01004	.8	.00025
.9	.380	.9	.197	.9	.09492	.9	.03826	.9	.00987	.9	.00023
43.0	.378	54.0	.196	65.0	.09423	76.0	.03789	87.0	.00971	98.0	.00020
.1	.376	.1	.195	.1	.09355	.1	.03753	.1	.00955	.1	.00018
.2	.373	.2	.194	.2	.09287	.2	.03717	.2	.00939	.2	.00016
.3	.371	.3	.192	.3	.09220	.3	.03681	.3	.00924	.3	.00015
.4	.369	.4	.191	.4	.09153	.4	.03645	.4	.00908	.4	.00013
.5	.367	.5	.190	.5	.09086	.5	.03609	.5	.00893	.5	.00011
.6	.365	.6	.189	.6	.09020	.6	.03574	.6	.00878	.6	.00010
.7	.363	.7	.188	.7	.08954	.7	.03539	.7	.00863	.7	.00009
.8	.361	.8	.186	.8	.08888	.8	.03504	.8	.00848	.8	.00007
.9	.358	.9	.185	.9	.08823	.9	.03470	.9	.00833	.9	.00006
44.0	.356	55.0	.184	66.0	.08758	77.0	.03435	88.0	.00818	99.0	.00005
.1	.354	.1	.183	.1	.08693	.1	.03401	.1	.00804	.1	.00004
.2	.352	.2	.182	.2	.08629	.2	.03367	.2	.00789	.2	.00003
.3	.350	.3	.181	.3	.08565	.3	.03333	.3	.00775	.3	.00002
.4	.348	.4	.180	.4	.08501	.4	.03299	.4	.00759	.4	.00001
.5	.346	.5	.178	.5	.08438	.5	.03266	.5	.00747	.5	.00001
.6	.344	.6	.177	.6	.08375	.6	.03233	.6	.00733	.6	.00000
.7	.342	.7	.176	.7	.08313	.7	.03200	.7	.00720	.7	.00000
.8	.340	.8	.175	.8	.08250	.8	.03167	.8	.00706	.8	.00000
.9	.338	.9	.174	.9	.08188	.9	.03135	.9	.00693	100.0	.00000

tion 1, we may calculate the F value of a mixture of dyestuffs (Fm), and hence the reflectance of the mixture dyeing at the specified wavelength, provided we know the spectrophotometric curves of the components at a specified concentration, and the concentration of each of the components in the mixture. If calculations of this equation are made at a sufficiently large number of wavelengths, then the spectrophotometric curve of the mixture can be predicted.

The accuracy of equation *(1)* is quite good when calculations are made for wool dyeings. Calculations for acetate rayon dyeings, and for vat dyes pigment padded on cotton are also fairly accurate. Inaccuracies for nylon dyeings and application of certain direct dyestuffs on cotton may be so great as to render the equation almost useless. In these cases, the dye components for matching the standard may be chosen by spectrophotometric curves, but the required amounts will have to be established more by trial and error methods than by calculations.

When equation *(1)* is to be used in matching a curve with a given set of dyes, all of the values in it are known with the exception of a, b, c, . . . Thus if five dyestuffs are to be used in matching the curve, there are five unknown quantities. We might solve for these five unknowns by writing in the values of equation *(1)* at five different wavelengths and thereby set up five equations to be solved simultaneously. This method, however, is cumbersome in most cases, and a much simpler solution may be used.

TRIAL CALCULATIONS

In order to use equation *(1)* for calculation of the required amount of each of the components, let us arbitrarily choose eight wavelengths spaced more or less evenly across the spectrum. These wavelengths are specified in Table II which also lists the F values for the chosen dyestuffs. All F values were obtained simply by noting the reflectance of the appropriate spectrophotometric curve at the specified wavelength and converting it to the F value by means of Table I.

Let us now write equation *(1)* in the correct form for calculation of the first of the specified wavelengths, 420 mμ. We will substitute in the proper F-values from Table II, and for A, B, C, etc we will substitute the concentrations specified in the table. The resulting equation is

$$6.725 = \frac{a}{.25} \times 5.700 + \frac{b}{.5} \times 10.134 + \frac{c}{2.0} \times 5.704 + \frac{d}{.5} \times 2.113 + \frac{e}{.5} \times .926 + 0.412 \times \left(1 - \frac{a}{.25} - \frac{b}{.5} - \frac{c}{2.0} - \frac{d}{.5} - \frac{e}{.5}\right) \quad (2)$$

TABLE II
F VALUES AT SPECIFIED WAVELENGTHS

Dyestuff and Concentration	Abbreviation	Wavelength (Millimicrons) 420	460	500	540	580	620	640	680
Standard		6.725	6.178	4.311	2.303	1.088	0.477	0.317	0.129
Fast Light Yellow GGXN (0.25%)	GGX	5.700	2.205	0.336	0.121	0.152	0.052	0.046	0.034
Fast Light Orange GA (0.5%)	GA	10.134	10.134	15.682	1.383	0.075	0.031	0.024	0.017
Fast Light Red BA (2%)	BA	5.704	10.134	24.010	32.341	6.725	0.400	0.133	0.050
Victoria Fast Violet RRN (0.5%)	RRN	2.113	2.205	3.814	7.363	9.025	4.925	2.205	0.299
Alizarine Blue SAP (0.5%)	SAP	0.926	0.869	1.289	2.641	4.925	6.725	6.725	3.405
Tartrazine C Extra (0.5%)	C	13.303	11.520	1.868	0.105	0.057	0.038	0.034	0.025
Undyed Wool		0.412	0.208	0.133	0.098	0.075	0.056	0.048	0.031

TABLE III
FIRST TRIAL CALCULATION

Dyestuff	% Conc	Wavelength (Millimicrons) 420	460	500	540	580	620	640	680
SAP	.01	.018	.017	.026	.053	.099	.135	.135	.068
BA	.11	.314	.507	1.320	1.780	.370	.022	.007	.003
GA	.10	2.040	2.030	3.160	.278	.014	.006	.005	.004
GGX	.19	4.340	1.672	.254	.159	.116	.040	.035	.026
RRN	.03	.128	.133	.229	.255	.544	.296	.133	.019
Sum (F_M)		6.840	4.359	4.989	2.525	1.143	.499	.315	.120
R (%)		6.4	9.4	8.4	14.5	24.8	38.2	46.1	61.5

where a, b, c, d and e are the percentages of each of the components GGXN, BA, RRN and SAP, respectively, that will be placed on the cloth to make the required match. (Note that a, b, c, etc are not percentages of each component in the mix, but percentages by weight on the cloth.) Similar equations may be written for the relationships at other specified wavelengths.

Results of the first trial calculations are shown in Table III. Concentrations of the components were estimated rather than calculated, after which the estimates were checked by the calculations. We know, for example, that the F value of the standard at 680 mμ (0.129) must be made up mostly from the F value of SAP, and that the F value of 640 mμ (.317) must be made up from both SAP and RRN. From this information we can make a fair estimate of how much SAP and RRN is required. In a similar manner, at 580 mμ the required F value of 1.088 must be made up mostly from the contributions of RRN, SAP and BA. A few estimations and corrections suffice to make the first trial calculations given in the table. Note that the last term of equation *(2)* has not been included in the calculations. The reason for this is that the sum of the terms in the parenthesis is close to zero and since this sum is multiplied by a small value (F_o for the undyed wool), it is negligible in comparison with the large values of F required for matching the standard. The values of F_M have been converted back to reflectance (R) by use of Table I.

A plot of the calculated reflectance (R) for the mixture described in Table III is shown in Figure 9. The eight points which were calculated in Table III are indicated by small circles, and a smooth curve has been drawn through them. This curve should be compared with that shown by the solid line in Figure 1, which is the one we are trying to match. Note that the very serious humps in the curve for a daylight match only, shown by the dashed line in Figure 1, no longer exist. There is still, however, an unwanted dip in Figure 9 at 400 mμ and a hump at 460 mμ. This suggests that we have not chosen the proper yellow. GGX, as may be seen by Figure 4, increases in absorption at shorter wavelengths, whereas the curve we wish to match, Figure 1, decreases in absorption (increases in reflectance) from about 430 mμ to 400 mμ. The curve for Tartrazine C, Figure 7, shows characteristics more nearly like those of the curve we wish to match in the range of 400 to 430 mμ. Let us therefore substitute Tartrazine C for Fast Light Yellow GGX and make a second trial calculation.

Results of the second trial calculation are shown in Table IV. The concentrations of the dyestuffs used are the same as those used in Table II except that 0.19% of GGX has been replaced with 0.16% of C. Results of the second trial calculations are shown in Figure 9 by small squares. A smooth dashed line has been drawn through these points. Note that use of Tartrazine C has smoothed the curve so that its shape is very similar to that desired, Figure I. We

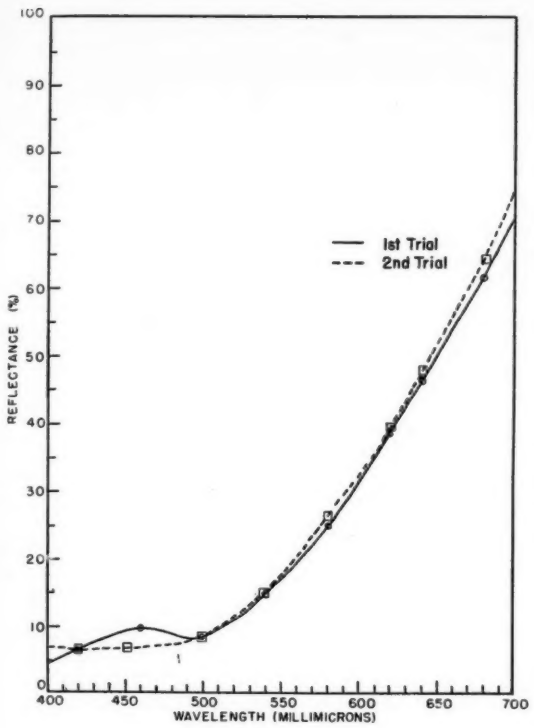

Figure 9
1st and 2nd Trial Calculations

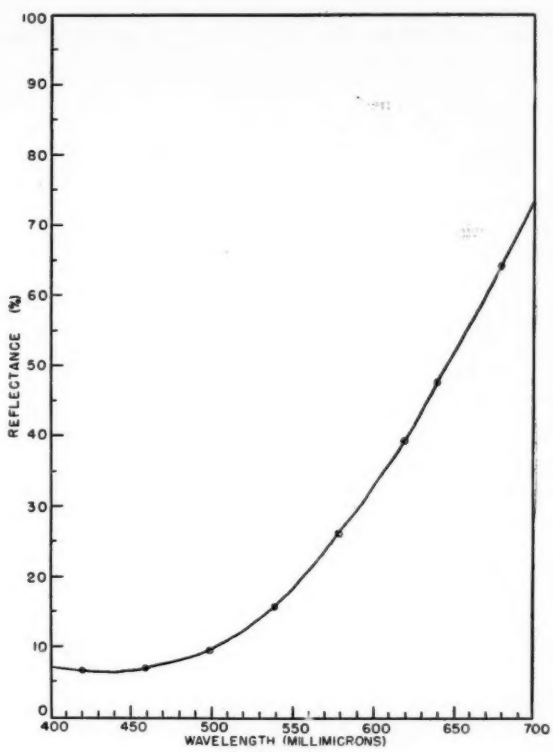

Figure 10
Final Trial Calculations

might calculate a slightly better match by increasing the reflectance at 500 mμ and decreasing it at 680 mμ. A change in the orange and yellow components will raise the curve at 500 mμ without serious change at other wavelengths, but we cannot lower the curve at 680 mμ without causing serious trouble at other points. We might look for a substitute for SAP, but the only suitable acid dye that produces a lower reflectance at 680 mμ is Alizarine Supra Blue SESN. For reasons other than color, however, we did not wish to use this dye.†

The final trial calculation of the mix is given in table V and plotted in Figure 10. The accuracy of the method does not warrant calculation of a more accurate match. In fact, the second trial calculation would probably have been sufficient.

The calculations so far described require less than two hours for completion. This includes choosing the components and assumes that the person making the calculation is sufficiently acquainted with algebra to understand the meaning of equation (2) and the method of using it as shown in Tables III, IV and V. After practicing with a few calculations, any intelligent high school student should be able to carry out the method with success, but final choice of the components, of course, should be made only by a colorist or dyer acquainted with the properties of the various possible dyestuffs.

Different methods of carrying out these calculations might have been employed. Instead of choosing the wavelengths rather arbitrarily, we might have chosen them on the basis of the maximum absorption (minimum value of R) for each of the dyestuffs used. And as pointed out above, we might have solved for a, b, c, d and e (the concentration of each component to be used in the mixture) by solving five equations simultaneously. Furthermore, several workers have suggested functions of R other than $(1\text{-}R)^2/2R$ as being more accurate. It is doubtful, however, whether the use of the more refined methods contribute anything

† Incidentally, Alizarine Supra Blue SESN is particularly noted because it is one of the few light-fast acid blues which go markedly green in tungsten light. It goes green because it has an unusually low reflectance from 680 to 700 mμ. If this dyestuff were chosen for use here, however, it would not be because of previous knowledge of its characteristics, but because a glance through the file of spectrophotometric curves shows it to have the desired reflectance characteristics.

TABLE IV

SECOND TRIAL CALCULATIONS

Dyestuff	% Conc	Wavelength (Millimicrons) 420	460	500	540	580	620	640	680
SAP	.01	.018	.017	.026	.053	.099	.135	.135	.068
BA	.11	.314	.507	1.320	1.780	.370	.022	.007	.033
GA	.10	2.040	2.030	3.160	.278	.014	.006	.005	.004
C	.16	4.260	3.690	.598	.034	.018	.012	.011	.008
RRN	.03	.128	.133	.229	.255	.544	.296	.133	.019
Sum (F_M)		6.760	6.377	5.333	2.400	1.045	.471	.291	.102
R (%)		6.5	6.8	8.0	15.0	26.1	39.2	47.5	64.0

TABLE V

FINAL TRIAL CALCULATIONS

Dyestuff	% Conc	Wavelength (Millimicrons) 420	460	500	540	580	620	640	680
SAP	.01	.018	.017	.026	.053	.099	.135	.135	.068
BA	.11	.314	.507	1.320	1.780	.370	.022	.007	.003
GA	.07	1.430	1.420	2.200	.195	.010	.004	.004	.003
C	.18	4.790	4.040	.674	.038	.020	.013	.012	.009
RRN	.03	.128	.133	.229	.255	.544	.296	.133	.019
Sum (F_M)		6.680	6.117	4.449	2.321	1.043	.470	.291	.102
R (%)		6.5	7.0	9.3	15.5	26.1	39.2	47.5	64.0

to the accuracy of the final match. It may be that the initial calculations would be slightly more accurate, but since a correction calculation may be performed after the first trial dyeing, as described below, this added accuracy is of doubtful value when compared with the added complexity of other methods.

A trial dyeing made according to the dyebath formula specified in Table V must now be made. The spectrophotometric curve of this dyeing is shown as a dashed line in Figure 11. The solid line is the curve of a 1% dyeing of the standard we are trying to match. Inaccuracies in the method of calculation account for the discrepancies between the predicted curve of Figure 10 and the curve actually obtained in Figure 11. Visually, the match between the standard and the first trial dyeing is not good, but it is closer than one would expect even an experienced dyer to obtain on his first trial dyeing using five components. The important point, however, is that the two colors shown by the curves of Figure 11 change in the same manner and by about the same amount when examined under different illuminants. This means that the components have been properly chosen for color, and the only corrections needed are in the amount used.

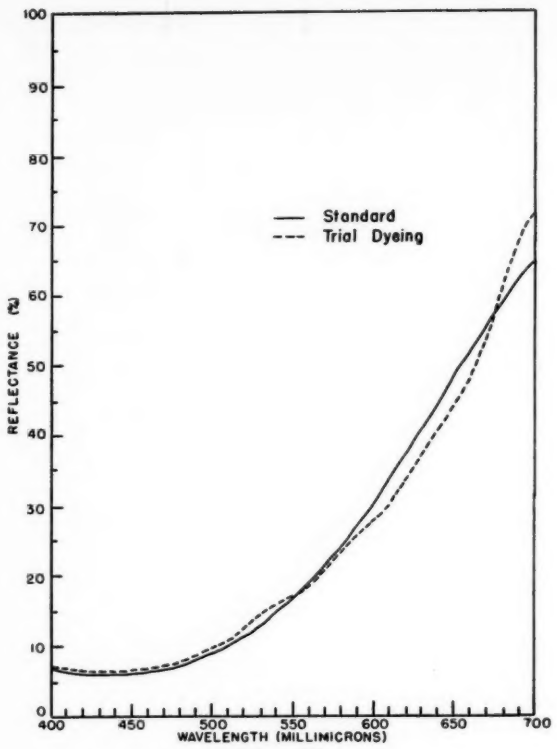

Figure 11
First Trial Dyeing

CALCULATION OF CORRECTIONS

The differences in color between the dyeing made according to the calculated dyebath formula and the color desired might be decreased in either of two ways. We might rely entirely upon the trained colorists' skill in estimating the required changes in the formula, or we might calculate the required changes. If the former course is adopted, the colorist must be warned that any changes in components used will cause changes in the spectrophotometric curve, and hence may destroy the desired color change in artificial light. Any changes in the amounts of each component must be made so as not to cause large changes in the ratio of one component to another. As long as the spectrophotometric curve of the mixture dyeing is available, however, the method of calculating the correction may usefully be employed.

Calculation of the corrections is carried out by a difference method. First we calculate the difference between the desired and obtained F values, then alter the concentrations so that the differences in calculated values between the old and new formulations are equal to the differences between desired and obtained F values. This process is described more clearly in Table VI. The first row of the table gives the desired F values and the second gives those actually obtained. Both sets of values were taken from the data given in Figure 11. Note that the first row in this table should, ideally, be identical with the first row in Table II. It is different because small differences in the dyeing conditions produce differences in color between two dyeings of the same dyebath formula. The dyer allows for this by always making a dyeing of the standard and sample together. We will follow the same procedure.

In the third row of Table VI, the difference in F values between the desired and obtained shades is given. These values must be added to the F values we expected to get (those given in Table V) and this sum, which appears as the fifth row of Table VI is the corrected set of values which the corrected dyebath formulation must match. A dyebath formula which gives F values closer to the corrected values is also shown in Table VI. Note that the blue component has been decreased and the red, yellow and orange increased in comparison with the dyebath formula given in Table V. The reason for this alteration is that we wished to increase the F values at wavelengths of 420, 460, 500 and 540 mμ, but wished to decrease F values at wavelengths of 580, 620, 640 and 680 mμ.

A second dyeing must now be made according to the dyebath formula given in Table VI. The spectrophotometric curve of this second dyeing is shown as a dashed line in Figure 12 and a dyeing of the standard is shown as a solid line. Visually, this is a fairly good match with the standard, but it can be improved. The blue and violet components appear to be about right, but the concentration of red, yellow, and orange must again be increased. At 680 mμ the desired curve is far below the curve we have obtained, but increasing the blue or

TABLE VI

FIRST CORRECTION CALCULATIONS

	Wavelength (Millimicrons)							
	420	*460*	*500*	*540*	*580*	*620*	*640*	*680*
a) Desired	7.096	6.844	4.601	2.452	1.187	.530	.346	.142
b) Obtained	6.387	6.178	4.050	2.205	1.245	.664	.445	.133
c) a) — b)	+.709	+.666	+.551	+.247	—.058	—.134	—.099	+.009
d) Expected	6.680	6.117	4.449	2.321	1.043	.470	.291	.102
Corrected Values (d) + c)).	7.389	6.783	5.000	2.568	.985	.336	.192	.093
SAP .005	.009	.008	.013	.026	.050	.068	.068	.034
BA .125	.356	.576	1.500	2.022	.420	.025	.008	.003
GA .08	1.635	1.625	2.513	.223	.011	.005	.005	.003
C .19	5.055	4.262	.711	.040	.021	.014	.011	.010
RRN .03	.128	.133	.229	.255	.544	.296	.133	.019
	7.183	6.604	4.996	2.566	1.046	.408	.225	.069

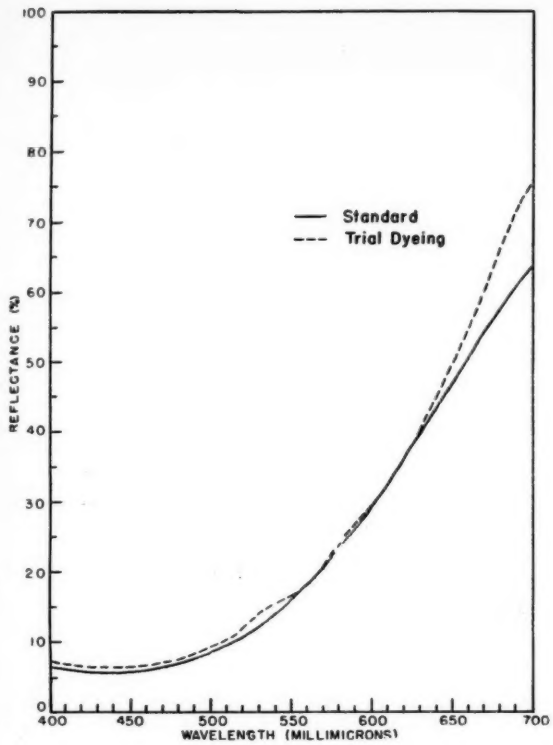

Figure 12
Second Trial Dyeing

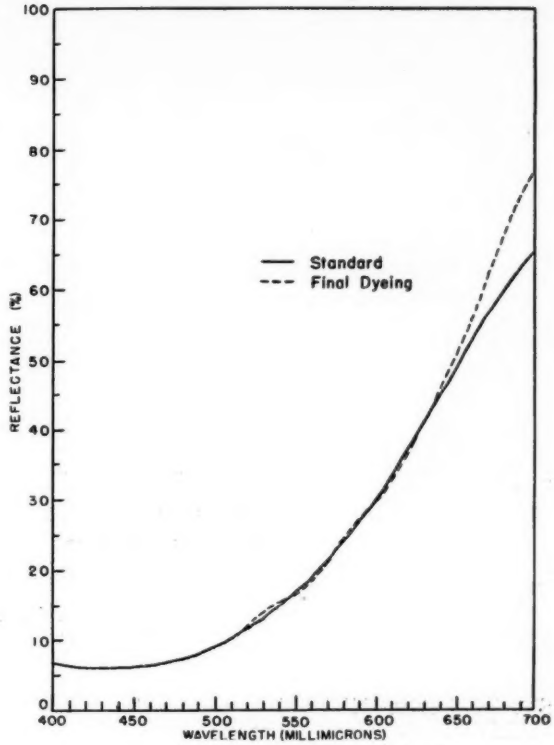

Figure13
Final Dyeing

violet concentration will merely produce the curve as shown in Figure 11. Neither the blue (Figure 6) nor the violet (Figure 5) dyes used absorb enough light at 680 and 700 mμ to correct this error.

Corrections to the formula given in Table VI have been calculated in Table VII. Exactly the same procedures have been used. The new formula requires no change in the blue and violet components, but calls for an increase in the concentration of the red, yellow and orange components

The spectrophotometric curve of a dyeing made according to the dyebath formula given in Table VII is shown in Figure 13 as a dashed line and the standard as a solid line. In view of the fact that the discrepancy between the two curves at wavelengths around 680 mμ cannot be corrected by changing the concentration of the components used without introducing other errors, further calculations using this method would be useless. The very small difference in color between the standard and sample can be corrected only by estimates based on either visual or tristimulus evaluation of the two colors. In fact, if a trained colorist were solving this problem, the first correction calculations would have been sufficient. On the basis of the second dyeing, he could have made a correction which would produce a match as good as, or perhaps better than, that obtained with the third dyeing (Figure 13).

Colorimetric evaluations of the various dyeings for both daylight (Illuminant C) and tungsten light (Illuminant A) are given in Table VIII. Note from the Munsell notation that the standard goes red in tungsten light whereas the dyeing shown by the

TABLE VII

SECOND CORRECTION CALCULATIONS

	Wavelength (Millimicrons)							
	420	*460*	*500*	*540*	*580*	*620*	*640*	*680*
a) Desired	7.800	7.363	4.925	2.617	1.262	.552	.367	.154
b) Obtained	6.725	6.725	4.423	2.324	1.163	.562	.336	.084
c) a) — b)	+1.075	+.638	+.502	+.293	+.099	.000	+.031	+.070
d) Expected	7.183	6.604	4.996	2.566	1.046	.408	.225	.069
Corrected Values (d) + c))	8.258	7.242	5.498	2.859	1.145	.408	.256	.139
SAP .005	.009	.008	.013	.026	.050	.058	.058	.034
BA .135	.385	.622	1.620	2.185	.454	.027	.009	.003
GA .09	1.840	1.830	2.830	.251	.012	.006	.006	.003
C .20	5.320	4.486	.748	.042	.022	.015	.012	.011
RRN .03	.128	.133	.229	.255	.541	.296	.133	.019
	7.682	7.079	5.440	3.759	1.082	.412	.228	.070

TABLE VIII

COLORIMETRIC EVALUATION OF SWATCHES

Dyeing	*Illuminant*	*X*	*Y*	*Z*	*x*	*y*	*Munsell* *Hue*	*Munsell* *Value*	*Munsell* *Chroma*
Standard (Fig 1)	C	.2397	.1994	.0768	.465	.387	4.6YR	5.02	7.2
	A	.2946	.2097	.0099	.573	.408	3.8YR	5.13	14.6
Three Component Match (Fig 1)	C	.2542	.2103	.0730	.473	.391	4.8YR	5.14	7.6
	A	.3018	.2226	.0048	.570	.421	5.0YR	5.27	14.9
First Trial Dyeing (Fig 11)	C	.2288	.1980	.0850	.447	.387	5.7YR	5.00	6.3
	A	.2769	.2046	.0132	.560	.414	4.5YR	5.08	13.5
Second Trial Dyeing (Fig 12)	C	.2425	.2030	.0825	.459	.385	4.6YR	5.06	6.9
	A	.2955	.2112	.0135	.568	.406	3.7YR	5.15	14.0
Final Trial Dyeing (Fig 13)	C	.2406	.1999	.0774	.465	.386	4.4YR	5.02	7.2
	A	.2967	.2100	.0102	.574	.406	3.6YR	5.13	14.6

dashed curve in Figure 1 goes green. Note also that the final dyeing shown by the dashed line in Figure 13 goes red in artificial light by the same amount as does the standard.

The methods described above are not the only ones which can be used. A log K/S cam, for example, has been developed by Calco for use with the spectrophotometer. This is sold under the name "R" cam by the General Electric Company. In some cases, use of this cam simplifies the method, particularly where only two or three component dyes are used. Mechanical aids of one kind or another may also be used. In principle, however, all methods are identical; they differ only in details.

CONCLUSIONS

In determining the value of the spectrophotometer for shade matching problems of this type, the following facts should be considered:

1. Choice of components and calculation of the first trial formula required less than two hours time. Calculation of the two corrected formulas required about 20 minutes each. In simpler problems, the required time would be much less.
2. No consideration whatsoever was given to the way in which either the standard or the components change in artificial light. All calculations and choice of components were based solely on the shapes of the spectrophotometric curves and properties such as fastness which were relevant to the specific problem.
3. A good match with type in both daylight and artificial light was obtained with the third dyeing. A trained colorist could have altered the formula slightly to obtain a perfect match in one more trial.

REFERENCE

(1) Kubelka, P and Munk, F, *Zeitschrift fur technische Physik* 12, 593 (1931); Seibert, C A, *Am Dyestuff Reptr* 34, 272 (1945); Snelling, H J, *J Soc Dyers Colourists* 63, 419 (1947) and *du Pont Technical Bull* 2, 1 (1946).

• PATENT DIGEST •

PAUL WENGRAF

STABILIZING NYLON FABRICS——Passage Through a Molten Metal Bath. G, 2, 04

U S Pat 2,563,394
(Cadgene—August 7, 1951)

The resistance of nylon fabrics to stretching, shrinking or creasing is said to be improved by passing the material (which may also be of vinyl- or cellulose acetate fibers) through a metal bath under controlled conditions.

The goods are introduced into a closed vessel (10), which is filled with an alloy, e g, Cd, Sb and Pb or Cd, Bi and Pb, and heated by coils (11) to a temperature below the fusing point of the fibrous material. The fabrics enter the closed vessel at slot (14), run over (17, 19, and 21) and leave the vessel at (15). It is important that adherent air particles be removed by pressing the goods against these rollers during the travel through the metal bath. Since the surface of the molten metal tends to oxidize, a zone of inert gas (preferably carbon monoxide) is established. The gas, which is introduced through pipe (26) is lighted at the top of exit (27). The burning flame serves to indicate an excess of the carbon monoxide atmosphere. Roller (17) may be replaced by an indented roller to exert a transversal tension on the fabric. One example calls for treating nylon for 10-12 sec in a bath at 115-130°C. Corresponding figures for treating cellulose acetate fabrics are 35 sec at 140°C.

References cited by the Patent Office:

US Pat 2,334,233 (Wood/1943): shaping any plastic material (e g, glue, gelatin, casein, cellulose derivatives) by handling the material in a hot inert liquid, or possibly a molten metal alloy. The plastic substance may be formed within the hot liquid or immediately after leaving the bath.

US Pat 2,346,208 (Du Pont/1944): increasing the elongation of stretched, high tenacity cellulose acetate yarns by bringing the moisture-free material, in substantially relaxed condition just below the softening point and at the same time maintaining the yarns under low tension.

US Pat 2,437,687 (Celanese/1948): an apparatus comprising a chamber heated by surrounding liquid for extruding molten polymer fibers. Solid particles are deflected to the heated walls by a conical grid formed of wire mesh. Heat is generated in a vessel filled with an alloy of equal parts of Pb and Sn.

US Pat 2,437,703 (Celanese/1948): an apparatus for extruding molten thermoplastic masses for filament production by introducing the solids below the surface of an inert liquid, preferably a molten alloy having a specific gravity several times that of the filaments.

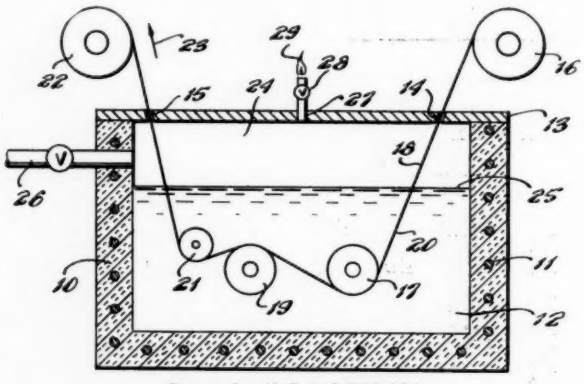

Figure 1—U S P 2,563,394

SHRINKPROOFING WOOL——Acrylic Acid- and Lower Alkylesters Combined. A, 2, 04

U S Pat 2,565,259
(American Cyanamid—Nyquist—Aug 21, 1951)

Wool or other protein-containing textiles are made shrinkproof according to earlier methods of treatment with chlorine-liberating substances, with permanganate or with resin forming components. These treatments are said to damage frequently the fiber material, to reduce the wearing qualities or to impart an undesirable harshness to the goods. Some of the

hitherto-used methods do not produce a durable effect and, in some cases, an increase in shrinkage after laundering occurs.

The present invention claims that a durable shrink resistance may be obtained by a treatment with organic solutions of acrylic acid ester monomers of the type CH_2=CH.CO.O-$OCH_2.CH_2O$-low alkyl; for example, ethoxyethylacrylate may optionally be combined with acrylates free of oxygen in the chain, such as ethylacrylate. The latter compound may either be omitted or added in amounts up to 90%. A polymerizing catalyst of the inorganic or organic peroxide type (Zn-, Ba-, Mg peroxide or diakylperoxides, acetyl peroxide, etc), persalts (e g, persulfates or perphosphates) and Co- or Mn naphthenates, etc, have to be added. Polymerization is effected *in situ* by volatilizing the solvent and heating the goods to elevated temperatures, i e, to 200-300°F. The resulting polymer is insoluble in water as well as in the usual organic solvents. An aftertreatment with formaldehyde after drying at low temperatures and followed by the curing operation may sometimes be necessary to develop the maximum shrink resistance.

The new method is said to have two advantages: (1) shrinkproofness is attained without impairing the natural soft touch of the wool substance and (2) the maximum effect is quickly reached and does not decrease after several launderings in contrast to former shrinkproofing processes.

Example: wool is treated with 60 p of a 10% toluene solution (containing 7.5 p ethylacrylate, approximately 2.5 p ethoxyethyl acrylate and .02 p benzoylperoxide, to which 5% of benzoylperoxide and a trace of cobalt naphthenate had been added previously. The goods are squeezed, dried on a frame and cured for 9 minutes at 290°F. Systematic tests using a modified AATCC standard method are said to have revealed superior effects after 5 washing cycles of 10 min each and after washing one hour in soap solution after each cycle.

References cited by the Patent Office:

USPat 2,406,958 (Du Pont/1946): stabilizing wool with an organic solution of an unsaturated hydrocarbon derivative (acrylonitrile or styrene) in the presence of iodine as a catalyst (cf *Am Dyestuff Reptr* 36,37,1947).

USPat 2,406,412 (Imperial Chemical Industries/1946): treating wool fibers, yarns or fabrics to improve the resistance to felting by exposing the material to the combined action of water vapors and a volatile vinylidene monomer, e g, methylmethacrylate.

USPat 2,343,093 (Du Pont/1944): resin dispersions that are substantive to nylon and cellulosic fibers comprise a stable aqueous solution of a polymerized vinylidene compound containing another resin and benzoylperoxide. Partly saponified polyvinylesters or alkylethers of cellulose are used as dispersing agents.

USPat 2,099,047 (Du Pont/1937): flexible articles of metal, paper or cloth may be produced by imbedding them in a plastic containing an interpolymer of methacrylic and acrylic acid esters.

Reference is further made to USPat 2,496,453-54 (Imperial Chemical Industries/1946) referring to a textile treatment with ethoxy ethyl methacrylate (cf *Am Dyestuff Reptr* 36, 99(1947)).

DYEING SUPERPOLYMER FIBERS of the Nylon Type Condensed with Hydrazine Derivatives C, 4, 07

Brit P 655,276
(Fisher, Wheatley—July 18, 1951)

The specification refers to the earlier Brit P 627,124, which covers the manufacture of superpolyamide fibers. These are fundamentally different from the known nylon polymers that are produced by condensing diamines with dicarboxylic acids. New fibers that exhibit improved dyeing properties have been prepared by condensing the components of superpolyamide fibers with dicarboxylic acid hydrazides, e g, adipic or sebacic acid hydrazides, in the presence of hydrazine. It can be assumed that the change in affinity of the new condensates is caused by the presence of acyclic amidine groupings at intervals in the polymeric chain. Under "acyclic amidine groupings" the simple amidine-group -C(NH)NH_2, the group -C(NH),-NH.NH_2, and other amine-substituted radicles of this type might be included.

The principal effect of these superpolymeric fibers is in their increased affinity to direct and other cotton dyestuffs. While nylon fibers have a rather poor affinity for some direct dyestuff brands, e g, Chlorazol Sky Blue FF, the fibers described in the present specification are dyed a very dark shade with this dye. The difference is all the more striking because the substantivity of the new fibers is said to be even greater than that of cotton or viscose rayon. Thus two-tone effects are made possible through the selection of appropriate dyestuff types.

Good results can also be expected with other dyestuff classes, e g, insoluble azo dyes developed on the fiber, and further, with (anthraquinoid) vat dyes, Indigosol- and sulfur dyes. Examples might include the following: direct dyes——Chlorazol Fast Scarlet 4 BS, and mixtures of direct dyes; vat dyes——Indanthrene Blue Caledone Blue RN; and sulfur dyes——Thional Brilliant Green GS.

Reference is made to reactions of hydrazine with other fibers. DuPont's USPat 2,497,526 (cf *Am Dyestuff Reptr* 39, 467, 1950) recommends the aftertreatment of polyacrylonitrile (Orlon) filaments with hydrazine to increase the affinity for acid dyes. Shrinkproofing effects are obtained by treating wool with hydrazine, according to USPat 2,382,632 (Ellis Foster).

ABSTRACTS

Elimination of Warp Streaks in Viscose Filament Linings.

L E Moody, *Canadian Textile J* 68, 52, Jan 19, 1951.

Warp streaks are primarily due to different warp yarns having different affinities for the dyestuff. The solution of the problem, as far as the dyer is concerned, is not to give a prolonged dyeing, where differences in absorption will accentuate the warpiness, but rather to cover it up as quickly as possible.

The writer's recommendation is to pad the dye in the greige, whenever loom stains and sizing will permit. With low end linings, dyeing from the greige is a necessity, for otherwise bad fraying or slipping occurs. However, in the case of linings which must pass rigid Government specifications for optimum fastness, desizing prior to dyeing is oftentimes a necessity.

Each dyer has his own likes and dislikes as to pad specifications. The writer prefers large diameter rolls (12-16") with density of 28-30° (Adams) for the top roll and 32° for the bottom roll. A hydraulic microset padder is to be preferred. The writer prefers the dip-nip method of padding, although some dyers use the slop-pad method, where the cloth enters directly into the nip. As much color as possible should be applied on the pad, at least 80 per cent of the shade. Six tons is good pad pressure. The wet pickup on the pad should be 60-65 per cent. Speeds of 75 to 125 yards per minute are satisfactory.

Dyestuff selection depends entirely on customer requirements for perspiration,

light, crocking, etc. In general, the low temperature direct dyeing colors do the best job covering warp streaks.

After padding at 140-160°F the goods are given four ends on the jig at 140°F, with Rapidase and salt to convert the sizing, and the addition of a non-ionic wetting agent. They are then given two more ends with salt at the boil, and dyeing is continued until the desired shade is reached.—WHC

Cellulose Acetate and Vat Dyestuffs.

G D Sutton, *J Textile Inst* 42, 538-48, August, 1951.

Even since the advent of cellulose acetate, work has been going on unceasingly to discover methods of dyeing it with dyes other than the usual dispersed water-insoluble dyes. The amount of work done during the last 25 years has been very great.

In earlier work the author discovered that unreduced water-insoluble vat dyes could be applied to cellulose acetate in the presence of a swelling agent, but that the depth of coloration obtained was not very great. On the other hand, if a reducing agent was present and the material was subsequently steamed, then the depth of coloration was considerably greater. Experiments were carried out therefore with the vat dye in the reduced state in the presence of a swelling agent.

Much work was done trying out various alkalis, many different swelling agents, reducing agents other than hydrosulfite, and various temperatures and times of dyeing. Many different vat dyes were tried out under varying conditions in the dye-bath.

Experiment showed that the use of ammonia as the alkali and sodium hydrosulfite as the reducing agent produced satisfactory reduction of a number of vat dyes, but that the dyes did not remain in reduction for very long periods after swelling agents has been added to the dyebath. The best results were obtained by substituting potassium carbonate.

Several water-soluble organic liquids used as the swelling agents for the cellulose acetate produced good results, but in general, industrial methylated spirits proved to be the best.

In dyeing of fabrics made of cotton or viscose and acetate, the concentration of the methylated spirit in the dye bath may be varied to control the degree of dyeing of the cotton or viscose in the fabric so that it is either substantially undyed or dyes tone in tone with the acetate.

Vat acids made by reducing certain vat dyes with caustic soda and hydrosulfite in the presence of a dispersing agent, and acidifying with an organic acid, may be applied to acetate to produce full shades at low temperatures. However, the cost of dyeing by this method is considerable.

Finally, the author developed a method for dyeing acetate from a bath containing an aqueous dispersion of an unreduced vat dye with an addition of sodium sulfoxylate formaldehyde. The temperature of the dyebath was 90-95°C. Sodium sulfite was added to keep the bath just on the alkaline side. The color yield and fastness to rubbing and washing were good. The addition of a dispersing agent was found to be helpful.

This process may be used to dye solid shades on mixtures of cotton or viscose and acetate. A similar method may also be used for printing acetate.—WHC

Enclosed-Jig Nylon Dyeing Offers Improved Light Fastness

F A Alter, *Textile World* 101, 244-50, October, 1951.

With the advent of woven nylon fabrics, the generally accepted method of dyeing synthetic fabrics in enclosed tensionless jigs with the dispersed acetate dyes was regarded as giving sufficient all-around fastness and brightness to enhance the marketability of the nylon end products also. But with new improvements in the methods of applying the acetate dyes on nylon, vat colors loomed as an even better long-term possibility for increased fastness in a good color range.

However, vat dyestuffs, applied in their usual manner as in cotton or rayon dyeing, were productive of only fair light and medium shades when used in ordinary hydrosulfite and caustic soda vat dyeing. Shades produced were dull, and their fastness evidenced none of the usual excellent characteristics found in other dyeings on cotton and rayon. Since vats showed possibilities of increased importance among the newer synthetic fibers, continued research was undertaken with these dyes on nylon and produced improved results by means of a change in the dyeing formula.

In this formula change, sodium hydrosulfite as a reducing medium in the vat bath was replaced by a more stable reducing agent, sodium sulfoxylate formaldehyde. With a change in temperature, starting at 170° F and raising to the boil, an increased affinity of nylon for the vat dye was observed. Darker shades of far superior fastness qualities were obtained. This change from the unstable hydrosulfite, which decomposes readily at higher temperatures, to the very stable sodium sulfoxylate formaldehyde allowed excellent reduction at increased temperatures in the dyeing operation. The results were much better fastness to crocking, rubbing, washing, and wet processing. While resultant lightfastness cannot quite measure up to that of ordinary vat dyeing of rayon and cotton, this newer method has made a decided improvement in nylon dyed with vat colors.—WHC

Fading of a Dye on Cellulose Acetate by Light and by Gas Fumes

M Couper, *Textile Research J* 21, 720-5, October, 1951.

In an effort to elucidate the chemical reactions that occur during dye fading on cellulose acetate fabric, a study has been made of the "fading products" isolated from faded dyeings of the compound 1,4-*bis*(methylamino)-anthraquinone. The dyed fabric was exposed in an Atlas FDA-R Fade-Ometer for 220 hours; to the sun for two summer months; and to gas fumes for three exposure periods, using the AATCC method.

The blue color of this dispersed-type dye became noticeably redder when, on the fabric, it was faded either by light or by gas fumes. The colored degradation products were extracted from the cloth with a mixture of benzene and methanol and were examined chromatographically. They were found to include each of the six possible 1,4-disubstituted anthraquinones containing methylamino, amino, or hydroxy groups. There was also evidence of the presence of anthraquinone nuclei bearing three or more hydroxy groups, and of imino and methylimino-anthraquinones.

The fading reaction in these cases is obviously complex, and includes *N*-dealkylation, hydrolysis of amino (or methylamino) to hydroxy groups, oxidation of amino to imino groups and of methylamino to methylimino groups, nuclear hydroxylation, nuclear deamination, and possibly oxidation of amino to hydroxylamino groups and of methylamino to *N*-methylhydroxylamino groups. A general oxidative pattern prevails.

The degradation products resulting from severe gas-fume fading of this dye on cellulose acetate bear a striking resemblance to those from light fading. Some deamination also occurs. Past studies of the chemistry of this type of fading have pointed to diazotization, nitrosation, and oxidation of amino groups, with subsequent decomposition influenced by light, water, and acids. The striking similarity between fume-fading products and those from light-fading places more emphasis on general oxidative action in gas-fume fading than previous evidence would suggest.

Comparative exposures, both to light and to gas fumes, were also made on nylon and acetylated nylon, dyed with this same dye. The approximately equivalent resistance to gas fumes of both the nylon and the acetylated nylon dyeings suggests that nylon confers gas-fume-resistance by some protective device other than through the basic nature of the amino end-groups in the nylon fiber.—WHC

(Additional Abstracts Appear on Page 31)

Proceedings of the
American Association of Textile Chemists and Colorists
Copyright, 1952, American Association of Textile Chemists and Colorists

JANUARY 7, 1952

30th Annual Convention
Dyeing Group——

ATTACHMENT OF DYES TO COTTON BY ETHER LINKAGE*

JOHN D GUTHRIE

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A method is described for coloring cotton by attaching certain azo dyes to the cellulose by ether linkage. Cotton fabric colored by this process has outstanding wash fastness. While the light fastness of colors so dyed is only fair, it is about equal to cotton fabrics dyed with commercial developed azo colors. Preparation of dyes especially suited to this method of application is described.

INTRODUCTION

RESEARCH on the attachment of aminoethyl groups to the cellulose of cotton by the use of 2-aminoethylsulfuric acid *(2)* indicated the possibility of using this type of reaction to attach other kinds of groups. For example, certain of the acetate dyes *(3)* contain the sulfatoethyl group, $-CH_2CH_2OSO_3H$. Although it seemed that the high molecular weight of these dyes or their stability in the strong sodium hydroxide required for the etherification reaction might present obstacles, a number of commercially available acetate dyes were nevertheless applied to cotton fabric by procedures similar to those found effective for aminization with 2-aminoethyl-sulfuric acid. In some instances the dyes were fixed to the fabric, but in only one case could actual union with the cellulose by ether linkage be demonstrated. This was the Solacet Fast Yellow GS**, which fortunately was soluble enough in strong sodium hydroxide solution to be applied by the one-solution method.

Since the exact structure of Solacet Fast Yellow could not be ascertained, a yellow sulfatoethyl dye was prepared by coupling 2-(*p*-aminophenoxy)ethylsulfuric acid with p-cresol by the method of A H Knight *(4)*. It reacted with cotton like Solacet Fast Yellow. Neither of these dyes, however, was quite as soluble in strong sodium hydroxide solution as was desired, and, furthermore, only light-yellow fabrics resulted from reacting them with cotton. Dyes of better solubility as well as those giving colors other than yellow were therefore sought. These were made by diazotizing 2-(*p*-aminophenoxy)ethylsulfuric acid and coupling it to substances having solubilizing phenolic or sulfonic groups or both, such as resorcinol, 2-naphthol-6-sulfonic acid, 2-naphthol-3, 6-disulfonic acid, 1, 8-dihydroxynaphthalene-3, 6-disulfonic acid and 1-amino-8-naphthol-4-sulfonic acid. Ether linkage of these dyes to cellulose when applied by curing with strong sodium hydroxide was demonstrated by decolorizing the fabrics with sodium hydrosulfite, diazotizing the decolorized fabrics with nitrous acid, and coupling with a phenolic substance either to restore the original color or to impart a different color.

Since these dyes are etherified to cotton under conditions similar to those used for aminization with 2-aminoethylsulfuric acid *(2)*, they may prove useful as additives to the aminization solution for the purpose of coloring the cotton and introducing amino groups simultaneously.

Previous methods for chemically attaching dyes to cellulose have involved stepwise processes, such as the production of partial aromatic amino ethers of cellulose, which were then diazotized and coupled with phenolic compounds. For example, Graenacher *(1)* etherified cellulose with o-, m-, or p-nitrobenzylchloride and related compounds, reduced the products to the amino derivatives, diazotized and coupled with phenolic compounds to produce colored products. Peacock *(5)* etherified cotton with m- or p-nitrobenzylphenyldimethylammonium chloride, reduced, diazotized and coupled to produce colored materials of good wash fastness but poor light fastness. In the method described in the present paper the dye itself is used as the etherifying agent and is attached to cellulose by ether linkage in a single operation.

EXPERIMENTAL

SOLACET FAST YELLOW GS——A solution of this dye was prepared by dissolving 600 mg in 60 ml of warm 20-percent sodium hydroxide. This solution was swabbed on sleeves of 80 x 80 (square) print cloth fitted over stainless steel beakers, which were then placed in a forced-draft oven at 110°C for 1 hour. After curing, the fabric was washed thoroughly with hot tap water. It was colored light-yellow. In other experiments on effect of time and temperature for this reaction, it was observed that about 20 minutes at 100°C was required to impart a noticeable yellow color to the washed fabric, but that darker shades could be obtained with longer times and higher temperatures. For ex-

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* Presented before the Dyeing Group at the 30th Annual Convention in New York on October 17, 1951. This paper constitutes a report of a study made under the Research and Marketing Act of 1946 in one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U S Department of Agriculture.

** The mention of trade products does not imply that they are indorsed by the Department of Agriculture over similar products not mentioned.

ample, curing at 120°C for 2 hours gave good results without noticeable tendering of the fabric. Breaking strength of the untreated fabric was 48 lb; while after reaction with the dye, the breaking strength was 45 lb for 80 warp threads. Although color was fixed to the fabric when sodium-hydroxide solutions ranging from 10 to 30 percent were tried, the 20-percent concentration gave the best results.

When fabric colored yellow by the above method was boiled for 6 hours in 1-percent sodium-hydroxide solution, only slight loss of color was observed. A severe wash test (45 minutes in the Launder-Ometer at 182°F with 0.5 percent soap, 0.2 percent Na_2CO_3, and 0.1 percent available chlorine, AATCC Standard Test Method 36-45 No. 4) removed little, if any, color.

In order to try this method of dye application on a larger scale, a roll of print cloth 12 inches wide, 10 yards long, weighing 378 g, was padded with a solution composed of 1106 g of water, 280 g of sodium hydroxide, and 14 g of Solacet Fast Yellow GS. It was necessary to warm the solution to about 60°C to dissolve all the dye. The pickup was 149 percent. After being padded the fabric was hung in a forced-draft oven at 110°C for 1 hour, washed thoroughly with hot tap water, air-dried, and ironed. A good uniform shade of yellow was obtained.

PREPARATION of 2-(*p*-aminophenoxy)ethylsulfuric acid——*p*-Nitrochlorobenzene, 64 g, was refluxed with 160 ml of ethylene glycol, 18.5 g sodium hydroxide, and 13 ml water for about 15 minutes; the hot mixture was poured into 320 ml of water and allowed to crystallize in a refrigerator. The crude product was filtered out, purified by extracting with boiling water, and allowed to crystallize. About 30 g of product was obtained, which was further purified by dissolving in ethyl ether and precipitating with petroleum ether to give 25 g of 2-(*p*-nitrophenoxy)-ethanol, mp 92°C. A portion of this, 18 g, was dissolved in ethanol and reduced with hydrogen in the presence of a platinum-oxide catalyst to yield 14 g of 2-(*p*-aminophenoxy)ethanol. A portion of this, 5 g, was sulfated by adding it a little at a time to 25 g of concentrated sulfuric acid cooled in ice-water. After the mixture had stood for 2 hours at room temperature, it was poured over 200 g of ice. After the ice had melted, the crystalline 2-(*p*-aminophenoxy)ethylsulfuric acid was filtered out and dried in a vacuum desiccator. It weighed 6 g.

PREPARATION OF DYES——In general the method of A H Knight *(4)* was used. 2-(*p*-Aminophenoxy)ethylsulfuric acid, 1 g, was dissolved in 13 ml of water and 1 ml of concentrated hydrochloric acid and diazotized at about 13°C with 0.3 g of sodium nitrite. After the solution was cooled to less than 5°C, it was poured slowly into an ice-cold solution of 0.47 g of *p*-cresol and 1.35 g of sodium carbonate in 9 ml of water. The resulting mixture was than warmed to 50°C, the dye was salted out by the addition of 1 g of sodium chloride, separated by filtration, and dried in a vacuum desiccator. The crude dye weighed 2.5 g and was very similar to Solacet Fast Yellow GS in properties and appearance.

Since it was thought that a dye with greater solubility in strong sodium hydroxide than the *p*-cresol dye just described would react better with the cotton, a dye was prepared by the procedure given above, but resorcinol was used instead of *p*-cresol. This resorcinol dye showed improved solubility in strong sodium-hydroxide solution and reacted with cotton fabric to give a yellowish-orange color. In a similar manner 2-(*p*-aminophenoxy)ethylsulfuric acid was diazotized and coupled with other phenolic substances to produce dyes of superior solubility in strong sodium hydroxide. The dyes prepared in this way that have been found suitable for attachment to cotton by ether linkage are summarized in the following table:

Coupling Agent	*Color When Etherified with Cotton Fabric*
p-cresol	yellow
resorcinol	yellowish orange
1,8-dihydroxy-naphthalene-3,6-disulfonic acid	purplish red
1-amino-8-naphthol-4-sulfonic acid	reddish blue
2-naphthol-3,6-disulfonic acid	red
2-naphthol-6-sulfonic acid	peach pink

To demonstrate the usefulness of the dyes as additives in the aminization process, 100 mg of the resorcinol dye was added to 10 ml of a solution composed of 65 parts of water, 25 parts of sodium hydroxide and 10 parts of 2-aminoethyl-sulfuric acid, and the colored solution was applied to fabric and cured for 1 hour at 100°C. After being washed, the fabric was orange-colored. The presence of amino groups was demonstrated by decolorizing with hydrosulfite and dyeing with Kiton Fast Red. The fabric dyed dark red, a characteristic of aminized fabric, while a control fabric, etherified with resorcinol dye alone and similarly decolorized, dyed very little with Kiton Fast Red.

To learn whether dyes containing the chloroethyl group,—CH_2CH_2Cl, would behave like the sulfatoethyl dyes, 2-(*p*-aminophenoxy)ethylchloride was prepared by the action of thionyl chloride on 2-(*p*-aminophenoxy)ethanol by the method of Ward *(6)*. This was coupled with resorcinol, with 1,8-dihydroxynaphthalene-3,6-disulfonic acid and with 2-naphthol-3,6-disulfonic acid to produce dyes. Only the first two were soluble enough in strong sodium hydroxide solution to be effective. When these were cured with sodium hydroxide on fabric they gave colors equivalent to the corresponding sulfatoethyl dyes, but of a slightly lighter shade. The curing time required was somewhat less than that found necessary for the sulfatoethyl dyes.

DECOLORIZING WITH SODIUM HYDROSULFITE AND REDEVELOPING——It is known that reductive cleavage of an azo compound with sodium hydrosulfite results in the formation of two amines. From this it was reasoned that decolorization with hydrosulfite of cotton colored by etherification should leave the 2-(*p*-aminophenoxy)ethyl group attached by ether linkage, and that it should therefore be possible to diazotize the decolorized fabric and to restore the color by redevelopment with a phenolic compound.

The yellowish-orange fabric that had been etherified with the resorcinol dye was decolorized with heat in a solution of 5 g of sodium hydrosulfite in 1.5 liters of water for 1 hour and 15 minutes at about 90°C. After being washed, the decolorized fabric was placed in a solution composed of 1 g of sodium nitrite, 200 ml of water, and 5 ml of concentrated hydrochloric acid for 10 minutes at about 13°C and then transferred to an ice-cold solution composed of 1 g of 2-naphthol-3, 6-disulfonic acid, 200 ml of water and 5 g of sodium carbonate. After 30 minutes the fabric was washed. It was colored an orange shade of red. Similarly, when the decolorized fabric was diazotized and developed with β-naphthol, a brilliant orange color was obtained. *p*-Cresol yielded a yellow color, and 1,8-dihydroxynaphthalene-3,6-disulfonic acid, a red color. In the same way, fabric etherified with the *p*-cresol dye was decolorized with sodium hydrosulfite and developed with various representatives of the Naphthol AS series to produce pink-colored fabrics. It was also observed that the diazotized fabrics retained their ability to couple after being washed with distilled water and dried in air. As a control on this series of experiments, cotton fabrics dyed by use of Naphthol AS coupled to Bordeaux Salt, Red Salt, and Scarlet Salt yielded no color when they were stripped with hydrosulfite, reacted with nitrous acid, and treated with 2-naphthol-3,6-disulfonic acid.

Since it was possible to develop color on fabric decolorized with hydrosulfite, it seemed likely that similar results could be obtained by etherifying the fabric with 2-(*p*-aminophenoxy)ethylsulfuric acid or the corresponding chloro-compound and then diazotizing and coupling. However, the two compounds were not soluble enough

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30th Annual Convention
Printing Group —

THE USE OF RESINOUS-COPPER COMPLEXES IN PRINTING*

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This paper concerns itself with both the discharging and the application printing of those direct colors which may be benefited by an after treatment with a resinous-copper complex. Processing problems are discussed and methods are suggested by means of which clear whites and prints with excellent fastness properties are obtained.

INTRODUCTION

SINCE the discovery of the first dye in 1884, our chemists and colorists have tried to perfect a simple method of coloring cellulose by direct means which will offer the highest possible fastness to light, washing, and perspiration. New dyestuffs have been developed, and after treatments, such as formaldehyde and acetic acid, chrome, copper sulfate, and many combinations of metallic salts, have proved to be of benefit, but until lately, none gave sufficient improvement to be of real value. However, a recent discovery has created a range of selected direct dyestuffs which, when aftertreated according to a new technique, may, on occasions, replace the more expensive vat dyes if fastness to chlorine is not of paramount importance.

THE AFTERTREATING METHOD

The new method of fixing direct dyes employs a resinous-copper complex in which the copper is incorporated within the resin molecule. Its use produces a tremendous increase in fastness. Tests on goods dyed or printed with direct colors that have not been treated show a considerable loss of color and a bad staining of white cotton when washed at 140°F, but the same type of dyestuff when aftertreated with a resinous-copper complex shows little or no loss of color and no staining of cotton at this temperature. Certain selected combinations of dyes can produce satisfactory tests even at 160°F. Also, the fact that a tight bond is formed between the dye, the fiber, and the resinous-copper complex means that this increase in fastness is not destroyed even after several launderings.

ADVANTAGES——Because of this improvement in resistance to washing, to hot wet pressing, and to fulling, we now have a range of colors with good light fastness ranking between the vats and the directs as to washing properties. There are many applications in which fastness to washing is important but fastness to chlorine bleaching is not necessary. In such instances, the use of direct dyestuffs aftertreated with a resinous-copper complex is desireable because of the resultant lower cost and simplicity of application.

DIFFICULTIES——The printing of this range of dyestuffs, both the discharge printing of the aftertreated ground shade and the direct printing of colors that are to be later treated, has presented the considerable problem of poor discharges and stained whites. The chemical nature of the dyes has not lent itself to discharge work, and the combining of the copper in the dye complex and the sulfur of the reducing agent invariably produces a greyish or creamy white. In the aftertreatment of application prints, the resinous-copper complex itself stains unprinted portions of the goods and materially detracts from the crisp pleasant look customarily associated with this type of work.

Past investigations of the problem of discharging these aftertreated dyes have not been highly successful. Suggested methods have either failed to produce a clear white or are unworkable. It has been found, as noted above, that, when a resin-copper dye complex is discharged, a grey or creamy color is produced even though the dyestuff itself is perfectly dischargeable in its uncombined state. This discoloration is probably due to a combination of copper and sulfur during the reaction in the ager, and, as this stain is not removable by any practical method, the program with which this report concerns itself was instituted with the prime thought of preventing the formation of such a permanent stain. A sequestrant, or chelating agent, in this case a sodium salt of a synthetically prepared polyamino acid, added to the discharge paste proved to be most beneficial and with the help of known discharging assistants and solvents, a white was produced. It should be mentioned, however, that this white is by no means a fact upon leaving the ager, for at this point the printed areas of the goods are a deep, dirty grey and the washing procedure must be modified to remove this discoloration. To achieve this end, it has been found that the addition of small amounts of acetic acid and hydrogen peroxide to the detergent in the washer clears the stain without perceptibly affecting the undischarged ground shade. Thus satisfactory whites are made without extra processing or the use of hazardous chemicals.

The other aspect of the problem of using resinous-copper complexes in printing is that of producing aftertreated application prints without leaving a stain on the white, unprinted portion of the goods. This discoloration is characteristic of the complex itself and is very resistant to soaping. However, this condition may be corrected by only a slight change in the washing procedure. Printing is done in the usual manner with suitable dyestuffs selected for their solubility and compatability. Steaming may be carried out in a cottage steamer or in a slow ager, and aftertreatment, on the usual equipment, either a slop washer or an open-width soaper. Care must be taken that the initial rinsing in plain cold water is very thorough as any dyestuff or paste clinging to the whites will be fixed by the subsequent treatment. A mild soaping before this treatment may be necessary in the case of heavy shades or of insufficient rinse water. Aftertreatment with resinous-copper complex follows the rinsing, and the strength and temperature of the aftertreating bath is determined by those individual mill conditions that fix the time of immersion. If the immersion time is short, the bath must be concentrated and hot. Conversely, as on a slop washer, which can provide a long period of treatment, the strength and temperature of the bath may be quite low. A rinse should follow this treatment.

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30th Annual Convention

Auxiliaries and Testing Group——

PROGRESS IN WETTING AND REWETTING TEST METHODS*

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Leonard Shapiro

The most frequently used methods for testing wetting agents are sinking tests, which are excellent for rapid laboratory testing. These measure time for only one degree of wetting, however, except for those methods in which different weights of hooks are employed, for which there is a different degree of wetting for each weight of hook. For complete evaluation a rate-of-wetting curve is important, and the hydrometer method is the simplest for this purpose. Several hydrometer designs are discussed. Factors affecting correlation of hydrometer rate-of-wetting tests with other methods are discussed.

Rewetting tests by the loaded tape method are described. Rewetting speeds improve considerably with increasing immersion time and with increasing temperature of treating bath. Drying conditions are also important in the application of rewetting agents. Rewetting of a dry fabric containing rewetting agent is much accelerated by a rise in temperature of the water employed for rewetting.

INTRODUCTION

IN the evaluation of wetting agents, we seem always to be on the horns of a dilemma (or even "trilemma") in which nothing is so simple as it appears at first glance. It would seem reasonable to expect that the problem of predicting wetting effectiveness would be solved by the extremely simple expedient of measuring the surface tension by any of a number of methods available to the physical chemist.

EFFECT OF SURFACE TENSION—— Actually, while there is good general correlation between low surface tension and wetting ability (*1*), a number of factors combine to complicate matters. One author points out, for example, that a trace of stearic acid lowers the surface tension of water markedly, but does not impart wetting properties (*2*). Equilibrium interfacial-tension values for liquids are readily measurable by contact-angle determinations on drops, advancing surfaces, etc; and these tests correlate with spreading powers of solutions over solid surfaces. Thus, it looks as though we can fully determine the properties of the system by measuring static equilibrium surface tensions and contact angles. But, now comes the rub——in our physical measurements, we work on equilibrium values, but in most industrial operations, we are interested not in eventual equilibrium, but in the *rate* at which wetting out occurs. The rate is influenced by surface tension, interfacial tensions, surface roughness, distribution of air in porous materials, etc.

Bartholome and Schafer (*2*), as their explanation for the lack of simple correlation between surface tension and wetting speed, advance the fact that we are dealing with the *velocity* of wetting and not with an equilibrium value (Fig 1). Their explanation for many of the discrepancies is the fact that we are really interested in the *rate* at which surface tension is lowered at a freshly prepared interface and not the *equilibrium* tension usually measured. Since the concentration of surface-active agent is higher at the interface than in the body of the liquid (Gibbs adsorption isotherm), when a surface is disturbed or newly formed, a certain time must elapse before molecules can migrate to the surface again to reduce surface tension to its equilibrium value. The curves for surface tension vs age of surface are asymptotic, and the period for leveling off may be measured in minutes, hours, or even days. When a textile material is immersed in the liquid, this variable time required for the surface-active molecules to migrate to the interface must be added to the other variables influencing wetting time.

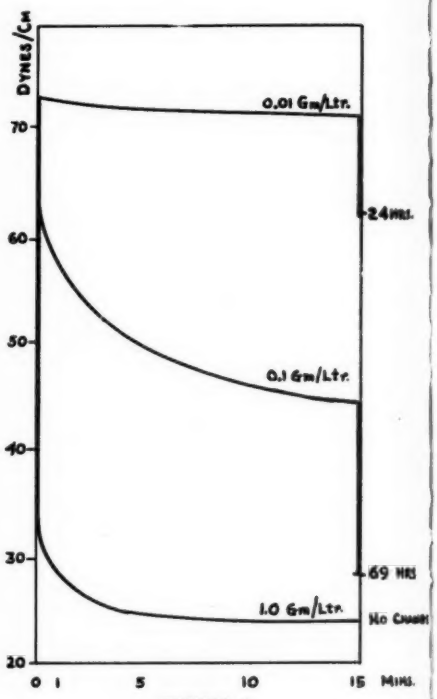


FIGURE 1
RATE OF SURFACE-TEMPERATURE LOWERING
(Bartholome and Schaefer)

Gruntfest (*11*) measured the rate of interface formation by the use of a hydrophil film-pressure balance. The wetting-agent solution was allowed to reach surface equilibrium. One-half was then disturbed by sweeping the surface clear with a straightedge, and the degree of unbalance was measured. Using 0.01% of Nacconal NR or Triton N-100, Gruntfest reported that 20 to 100 minutes was required to reach "zero unbalance." Thus, it is obvious that the equilibrium surface-tension values usually quoted in the technical literature are virtually useless in predicting wetting phenomena for textiles.

* Presented at the 30th Annual Convention in New York on October 19, 1951.

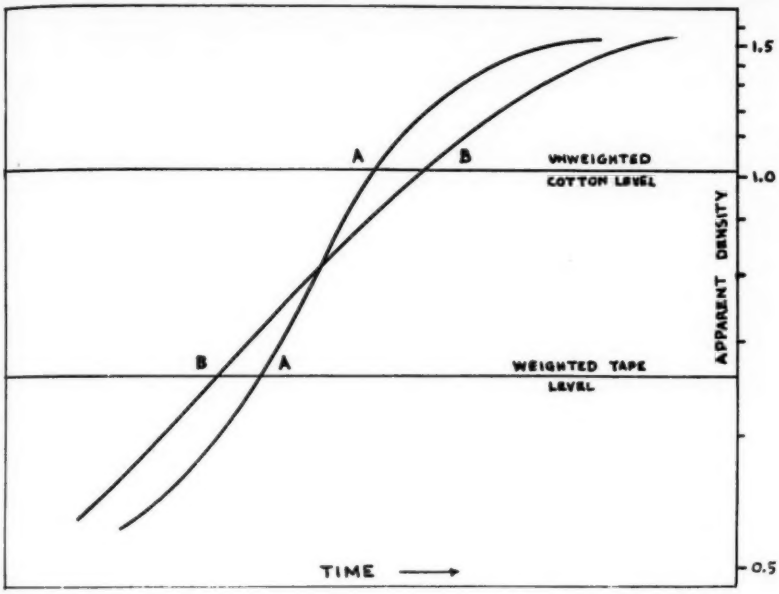


FIGURE 2

TYPES OF TEXTILE WETTING TESTS

Standard methods for measuring wetting effects on textiles are based on the sinking time of a piece of material deposited on the surface of a liquid or immersed therein. The most commonly used sinking test methods are

	Reference
1) Weighted material	
A) skein (Draves test)	(3)
B) tape	(4)
2) Canvas disc or square	
A) submerged patch	(5)
B) floating patch method	(6)
3) Rate-of-wetting tests	
A) hydrostatic balance	(4)
B) hydrometer method	(7)

While the above methods are often used in evaluating surface-active agents for applications other than textile, we must interpret the results with some reservation. Even in textile problems we must realize that we are testing the wetting out of *cotton* fibers, or, more specifically, of the thin layer of *cotton wax* surrounding the fibers. If we try to apply our conclusions to dewaxed or boiled-off cotton, or to wool, rayon, or synthetic fibers, we may find the results very misleading. However, the value of a standard reproducible test on readily available cotton materials should not be minimized.

DIFFICULTIES ENCOUNTERED IN CORRELATION OF TEST METHODS—Many investigators have been at a loss when confronted with the fact that, in a comparison of two wetting agents, product A may be better than product B by the canvas-disc method, but product B is better than A by the loaded-skein method (Draves test) with a particular hook. Actually, this is not so surprising, if we consider the complete rate-of-wetting curves. Thus, if the curves for A and B are represented by Fig 2, it is evident that B will sink faster than A by the Draves test (apparent specific gravity = 0.65 for a 3-g hook) but A will sink faster than B by the disc or patch test (apparent specific gravity = 1.00) where a larger proportion of air is displaced. In all cases where the curves cross between the degree of wetting obtained in the Draves test (a s g = 0.65) and that obtained by the patch tests (a s g = 1.00), this phenomenon is evident.

An even more astonishing type of crossover is that reported for different *concentrations of the same surface-active agent* (Fig 3). This effect was first reported by Gruntfest, Hager and Walker (7), and the results were so unbelievable that, for several years, little attention was paid to their paper, or to the implication that higher concentrations of surface-active agent produced faster initial wetting, but less complete wetting action in the long run than lower concentrations. This effect was confirmed by Reutenauer, Sisley and Dupin (9, in the issue before you) on tapes and skeins. Shapiro (4) confirmed the crossover effect using skeins, but not tapes, and speculated that the effect might be due to the physical disposition of the textile material to facilitate entrapment of air. Reutenauer et al (9) suggested that, with less wetting action, larger bubbles are formed, while, with larger amounts of wetting agent, smaller bubbles form and are entrapped in the fiber mass.

It is interesting to note, in the above connection, that some dyers have felt for a long time that good wetting agents are often poor "penetrants" and vice versa. In the light of the above findings, it looks as though this apparently unscientific belief may have some basis, since rapid initial wetting does not always indicate more complete final wetting (and may even be related to *poorer* final wetting). However, if, as suggested by Reutenauer, the small bubbles are actually detached from the surface, they would not interfere with dyeing, and this phenomenon

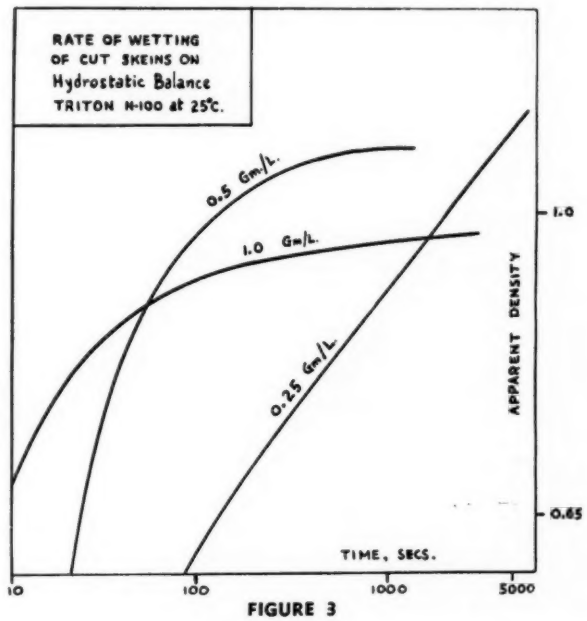


FIGURE 3

may be of no particular industrial significance.

This concept actually goes back a little further to the work of Stam and Petering (*10*) on the effect of wetting agents on the wetting out of wood blocks. These authors divide the wetting mechanism into a) surface spreading, b) capillary penetration and c) diffusion into cell walls. The curves for rate of water absorption actually show, in one case, the same crossover effect noted by Gruntfest et al. In general, they find that water absorption is not improved (or, in some cases, is slowed down) by wetting agents. Their explanation is that more rapid spreading over surfaces results in entrapment and compression of air in capillary spaces. Submerged blocks showed slower absorption than floating blocks for the same reason. They draw the interesting inference that these findings do not apply to textile materials in which *spreading* is of paramount importance and capillary penetration, of less importance.

The crossovers reported in the concentration-vs-degree-of-wetting curves for cotton indicate that Stam and Petering's work also applies, at least in some instances, to textiles, and Gruntfest (*11*) has recently reported that the mode of air displacement has a great effect on the eventual completeness of wetting. Thus, when the material is submerged rapidly, more air is entrapped and cannot get out, even in very long periods of time. When the samples are lowered into the liquid more slowly, air has a chance to escape and wetting is much more complete.

Many factors contribute to difficulties in relating Draves-test values or patch-test values with corresponding points on the rate-of-wetting curve. This is largely due to the fact that the curves are obtained on samples which differ from the Draves-test or patch-test samples in size, form and arrangement. Yarn tests cannot be correlated quantitatively with fabric tests, and fabric samples of different construction or size do not give comparable results. (The difficulty in obtaining standard lots of yarn or tape which behave alike for wetting tests is notable, even when the constructions are identical). In the previously reported hydrometer tests, the depth of immersion is much greater than in the Draves test, and the sample is twisted, or folded (*7*) or cut into smaller pieces (*9*). A portion of the work reported herein indicates that large variations in depth, as well as twisting, folding, or cutting the sample, all have a considerable effect on Draves-test results.

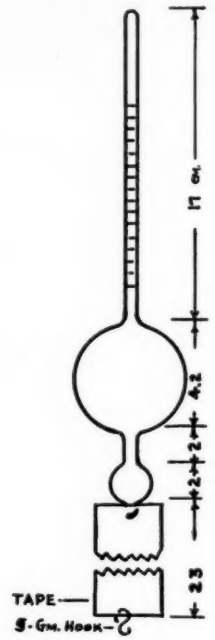
I EXPERIMENTAL PART—WETTING

THE HYDROMETER METHOD——In this investigation, attempts were made to determine some of the variables affecting the weighted-tape test, the surface-patch test, and the hydrometer test. The same tape fabric was used in all cases. Weighted-tape tests were run as described in the writer's previous paper (*4*) with 1-gram Monel-metal hook (weight of hook in water = 0.90 g). The hydrometer is the type used by Reutenauer, Sisley and Dupin (*9*) but was modified for use in a 1-liter graduate with a *single strip* of tape so as to duplicate, as nearly as possible, the weighted-tape test conditions.

The hydrometer was prepared by blowing a length of 6-mm Pyrex tubing to form two bulbs with a glass hook at the bottom (Fig 4). To use the hydrometer, the upper end of the 9" standard tape is fixed to the glass hook, and a 5-gram steel hook is inserted through the lower end. This serves to keep the tape and the hydrometer in a vertical position during the test.

The lower bulb of the hydrometer is weighted with mercury or lead shot, and an arbitrary scale is inserted in the hydrometer with a zero-point marked at the level reached with the hydrometer and hook only. At this level, the tape has zero effective weight (apparent specific gravity = 1.00).

Calibration of the hydrometer scale was accomplished by hanging 1-gram and 3-gram Monel-metal hooks from the hydrometer and determining the number of scale divisions with the hydrometer drops:



(Dimensions in centimeters)

FIGURE 4
RATE-OF-WETTING HYDROMETER

	Wgt in air	*Wgt in water**	*Scale Div*	*Scale Factor Divisions/g*
1-g hook.....	1.02	0.90	12	13.4
3-g hook.....	3.03	2.69	36	13.4

* From actual immersion-balance determination.

Readings below the zero mark are considered minus readings, those above zero are recorded as plus. The hydrometer, with tape and hook weight attached, is lowered rapidly (in about ½ to 1 second) into the wetting-agent solution in a 1-liter graduate. The operator reads the hydrometer scale as rapidly as possible while an assistant records the time and the readings. After a few minutes, wetting action slows down sufficiently so that one operator can read and record the results. Readings were continued for at least 75 minutes.

Solutions were prepared by adding a stock 5% wetting solution to tap water at 25°C, softened with Versene. The results were plotted on 4-cycle semilog paper directly using the arbitrary scale readings or converting first to apparent specific gravities.

Smooth curves are so readily obtained by this method, that one is apt to lose sight of the fact that consistent results are not obtained unless all details are carefully standardized. Thus, for example, an uncorrected 0.1-gram variation in tape weight will displace the corresponding curve considerably

TABLE I

WEIGHTED TAPES VS 1-INCH SQUARES

Syntholite 170 in soft water at 25°C

Conc'n, g/l	*1*			*0.5*			*0.1*
	Tapes		*Squares*	*Tapes*		*Squares*	*Tape*
Graduate Capacity	*1000*	*500*		*1000*	*500*		*1000*
	19	18	52	30	28	142	186
	18	18	51	30	29	139	187
Seconds	19	18	51	31	28	142	180
	19	18	52	31	30	146	165
	19	18	51	28	29	145	165
	—	—	—	—	—	—	—
Avg	18.8	18	51.4	30	28.8	145	177
From Curve Intersections	19		88	32		220	190

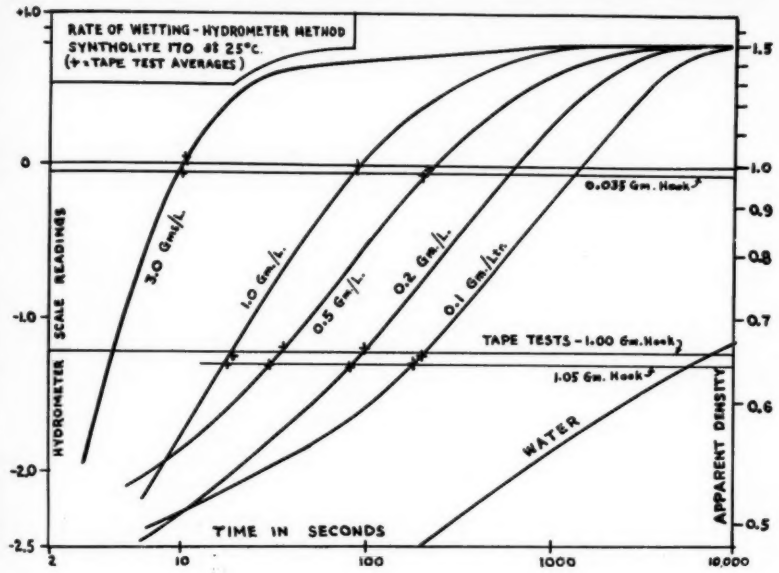


FIGURE 5

(results for each tape are converted to *apparent densities* before plotting, if tape weights differ).

The typical series of curves of Fig 5 show the effect of varying concentrations of a single wetting agent. Confirming the writer's previous results for tapes, the curves do not cross, and they all approach the same upper limit.

The advantage in adding upper limits for specific gravity of saturated cotton and lower limits for air at zero wetting is not so definite as might be expected. The upper limit is completely dependent on the specific-gravity constant for cotton, which in turn depends on the method of measurement. An excellent review of the subject is given by Stamm (*12*), who shows that the specific volume of cellulose varies with the type of fluid used to displace the air. Water gives the highest specific gravity since it swells the fibers, making smaller voids accessible to the water molecules. For water displacement on dry native cellulose, values of 1.60 to 1.61 seem most reliable, but for benzene displacement, the specific gravity is closer to 1.55. In this paper an arbitrary value of 1.60 has been indicated as an "upper limit", but it is evident from the accompanying graphs, that a specific-gravity of 1.50 would be satisfactory for these tests.

In a previous paper (*4*) the writer measured the volume of air per gram of cotton for tapes and skeins in water immediately after immersion and used this as zero-wetting point. This is interesting in a rough qualitative sense, but has the disadvantage that all the calculations are based on the highly uncertain "zero-second" readings. This makes it difficult to compare materials of different constructions, since it was previously shown that skeins entrap over 3.5 ml of air per gram of cotton (much of which is given off very rapidly in the form of large bubbles). Tapes, on the other hand, entrap only 1.58 ml of air per gram of cotton at the start. This is interesting in comparison with the measurements on void spaces in fabrics and yarns by Honold and Skau (*13*). On a range of oxford-weave fabrics they compute the volume of voids at 1.348 to 1.592 ml per gram (close to the 1.58 value found for grey tapes in water). They further report that the pore distribution shows a peak value of 7 microns for yarn, (5 microns for immature cotton) and this is reduced to 2 microns when the same yarn is woven into fabric (1 micron for immature cotton). Thus, it is not surprising that skeins and fabric strips behave quite differently in wetting tests.

CORRELATION OF RATE-OF-WETTING CURVES WITH WEIGHTED-TAPE AND FLOATING-SQUARE TESTS ——Weighted-tape tests and floating-square tests (same tape fabric throughout) were run to correspond to each of the concentrations of Fig 5.

The tape tests were run first in the standard 500-ml graduate (with 2 cm of initial height of liquid over top of tape) and then in the 1-liter graduate, where the initial height of liquid over the top of the tape was 10.5 cm (cf 10.5 cm at start and 16.5 cm at end for hydrometer test).

The sinking time for loaded tapes is evidently affected slightly by the liquid head acting above the tape, and sinking was about 4% slower at the greater depth. The sinking time in the 1-liter graduate was nearly equal to that read from the intersection of the curves of Fig 5 with the 0.66-apparent-density line.

The 1-inch squares, however, sink in 30 to 35% less time than might be predicted from the intersection of the curves with the 1.0-density line, and this is not surprising since the geometry of the systems is so different. In the floating-patch test, the liquid enters through the lower surface of the fabric and from the cut edges. Air is displaced partly from the top surface and partly through the edges. Thus, even though the hydrostatic pressure is lower, the opportunity for air displacement is greater, and this more than offsets the smaller area of contact with the liquid phase. An interesting observation was that squares which touched the side of the beaker sank *faster* than those which were kept away from the sides, probably because of the fact that air is discharged through the fabric edge touching the glass or touching the bubbles at the side. When the fabric is in the center, water hinders the discharge of air on all sides.

Since it was obvious that the floating-patch test could not be correlated with the rate-of-wetting curves for tape, another set of tests was run with an essentially *unloaded* tape (1-gram hook replaced by a 0.035-gram staple, resulting in an apparent density of 0.98, instead of 1.00). Results fall virtually on the rate-of-wetting curves in all instances.

It is interesting to note the close agreement of consecutive tests even for very long sinking times by the tape method. Confirming the previous test, the sinking was

TABLE II

UNLOADED TAPE TESTS @ 25°C IN SOFT WATER

Syntholite 170, g/l.....	3.0		1.0		0.5	
Capacity of Graduate, ml.....	1000	500	1000	500	1000	500
	11	9.5	89	87	223	207
	10.5	10	88	87	215	205
Seconds	11	9.5	87	91	205	206
	10.5	10	90	89	220	203
	10	10.5	89	86	214	201
Average	10.6	9.9	88.6	88.0	215.4	204.4
Speed increase for 500-ml grad, %.....		6		0.7		5

slightly *faster* for the *lower hydrostatic* pressure obtained in the 500-ml graduate (1- to 2-cm head). This is probably due to the fact that the difficulty encountered by air bubbles in escaping increases with the pressure exerted by the surrounding liquid.

(An illustration of the manner in which conflicting results may be obtained because of insufficient attention to minute details is the fact that the first tests on loaded tape showed exactly the reverse effect. Wetting speeds were slightly faster in the 1000-ml graduate. A careful check revealed that the hook used with the 1000-ml graduate weighed 1.05 g, while the hook used with the 500-ml graduate weighed 1.00 gram.)

MECHANISM OF AIR DISPLACEMENT——Careful observation of the manner in which bubbles escape from a tape yields interesting information concerning the mechanism of wetting. First, it is surprising to find that very few bubbles escape from the plane faces or selvages of a tape. In fact, virtually no bubbles can be seen on the surface. Bubbles escape almost entirely from the upper cut edge of the tape and must work their way through the *interior* of the fabric to the top. For slower wetting speeds bubbles form on and escape from *only one or two points* on the upper edge, which probably mark paths of least resistance.

The largest bubbles are formed for the lowest concentrations of surface-active agent. At higher concentrations, the first portion of the air is released in large bubbles and the balance in smaller bubbles. At a concentration of 3g/l (Fig 5) the bubbles were extremely tiny after a few seconds and clung to the cloth, so that, on the first test, the curve leveled off at an apparent specific gravity of 1.4 and showed no change in 4000 seconds. When the tape was shaken to dislodge these bubbles, the value immediately reached 1.5. The test was repeated, but the solution was first heated to 60°C to release dissolved air, then cooled to 25°C. While the very fine air bubbles were still in evidence, not so many clung to the fabric (perhaps they dissolved in the water), and there was no difficulty in obtaining the results of Fig 5 without a crossover at $D_A = 1.5$.

The effect of bubble size is a very interesting confirmation of the explanation advanced by Reutenauer, Sisley and Dupin (9) to account for crossovers in their rate-of-wetting curves. They point out that for solutions of low wetting power, the air follows the yarns and fibers upwards to the top, where large bubbles are formed. In solutions of excellent wetting power, the air separates immediately into fine bubbles, which are mechanically restrained by the *wet-out* fibers. This air, they state, does not actually contact the cotton, is readily eliminated by agitation, and hence should cause no difficulty in practical mill operations.

TABLE III

EFFECT OF CUTTING TAPES ON SINKING TIMES

Syntholite 170 at 50°C in Soft Water

	Selvages Left Uncut		*Tapes Cut and Stapled 3 mm Apart*		*No. of Segments*
Wetting Agent, g/l	*1 gm/l.*	*0.5 gm/l.*	*1 gm/l.*	*0.5 gm/l.*	
Seconds	11.7	21.3	*10.3	*19	1 (uncut)
	11.2	21.9	8.5	16.5	2
	10.9	29.7	7.6	18	3
	11.9	25.3	...	...	4

* With 2 staples.

TABLE IV

EFFECT OF CUT TAPES ON SINKING TIMES

Syntholite 170 at 0.5 g/l at 50°C in Hard Water (38 ppm)

	Ht of Liquid Above Tape, cm	*Sinking Time, Seconds Tapes Apart*	*Together*
One 9-inch Tape on one 1-g Hook	1 to 2	19	..
	15	20	..
Two 4.5-inch Tapes on one 1-g Hook	2	15	24
	7.5	14	18
	15	15	..

There seems little doubt that, with the single strips of fabric employed in these tests, crossovers in the rate-of-wetting-vs-concentration curves do not occur (or occur only in the lower portion, $D_A = 0.5$, where accuracy is poor because of variations in speed of tape immersion and of oscillation of the hydrometer.)

The crossovers reported in all the previous work (*4,7,9*) have been in the apparent density range of 0.8 to 1.2 (reached in about 10 to 100 seconds by Gruntfest, but in over 10 minutes under Reutenauer's experimental conditions).

It is likely that, with skeins, or with fabrics which are arranged so that two surfaces come in contact with each other, the mechanism suggested by Reutenauer et al for entrapment of fine bubbles assumes much greater importance.

EFFECT OF CUTTING TAPES——Since

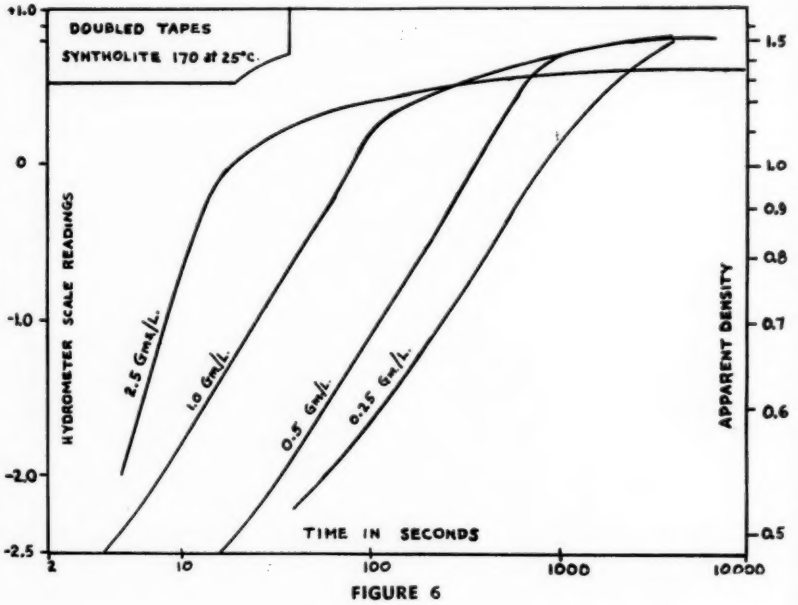


FIGURE 6

it was apparent that the air had to traverse the entire height of the tape before it could escape, it was felt that, if the tape was cut in various places at which air could escape, sinking times would be speeded up considerably. When 1, 2 or 3 horizontal cuts were made across the tape to leave a few selvage threads on each side to hold the tape together, no change in wetting speed was noted. When the tape was cut through completely and joined up again by means of staples, it was found that the air escaping from an upper edge was entrapped by the lower edge of the adjoining segment. This was overcome by separating the segments slightly and fixing them together with staples; marked reductions in wetting time were then obtained as shown in Table III.

With 1 *vertical* slit, the sinking time was reduced only to 11.1 seconds, and it was noted that very few bubbles escaped from the slit.

It is interesting to note that in the first series at ½ gram per liter, the wetting speed actually *decreases* with the number of cut edges since there are more points where air is trapped.

In the second series of Table III, the 3-mm spacing becomes much greater when the tape is immersed in the liquid under tension, and most of the bubbles actually escape at the cut edges. The decrease in sinking time is quite definite under these conditions.

The effect of cutting tapes and of having surfaces in contact with each other was illustrated by another series of tests run at several hydrostatic pressures. The tapes were cut in half and both halves were placed on the same 1-gram hook. The anchor string was adjusted to several different lengths to vary the hydrostatic pressure as shown in Table IV.

Table IV shows the following:

a) a definite increase in wetting speed due to cutting of the tape is caused by an increase in the number of edges from which air is released.

b) a marked *decrease* in wetting speed due to juxtaposition of two fabric surfaces.

RATE-OF-WETTING CURVES EMPLOYING MULTIPLE TAPES —— The preceding work on cut and doubled weighted tapes suggested that the increase in importance of capillary penetration over surface spreading should make it possible to obtain crossovers in the rate-of-wetting curves. For this purpose, hydrometer tests were run on doubled 4½-inch tapes (Fig 6) and tripled 3-inch tapes (Fig 7). In both these graphs, the curve for the highest concentration, 2.5 g/l, shows more rapid wetting at first, but levels off and crosses the others at an apparent density of about 1.35. Crossovers were not observed at 1.0 gram per liter or less.

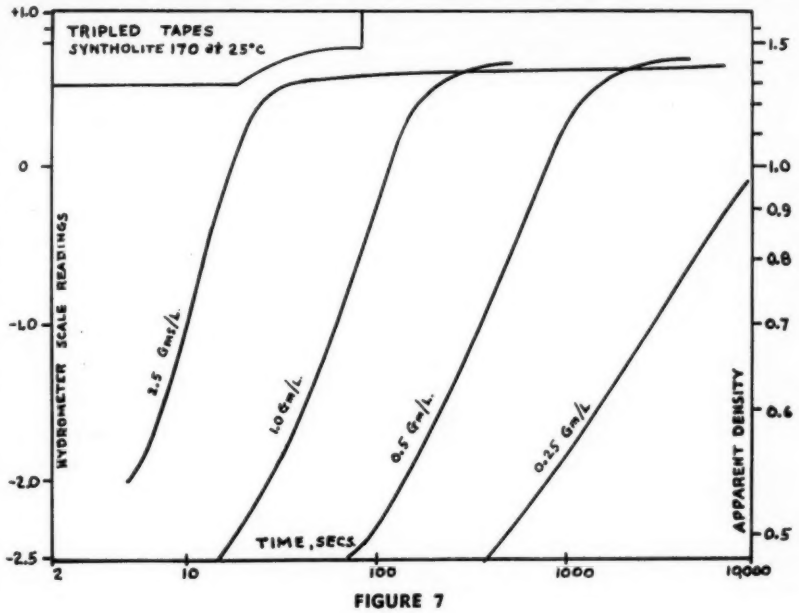


FIGURE 7

It seems likely that Reutemauer's fabric construction was such as to render capillary penetration more important (and, perhaps the larger doubled 7½ x 11½-cm samples contribute to this effect). This might accentuate crossovers and cause them to occur at slightly lower apparent densities. With skeins, crossovers are much more important and occur at much lower apparent densities.

It is interesting to compare the curves for single, doubled and tripled tapes (Fig 8) for a single concentration of surface-active agent. These shift toward the right, and their slopes increase as the number of plies of tape increases.

In explaining the crossovers in Gruntfest's rate-of-wetting curves, Schwartz and Perry (*14*) point out, with prophetic insight, that they must be caused by denser packing of the threads, which makes capillary action more important.

They further point out that, for contact angles of 0 to 90°, the rate of advance of a liquid into a capillary is *proportional* to the surface tension. In this case *higher* surface-tension promotes more rapid penetration, but *lower* surface-tension promotes more

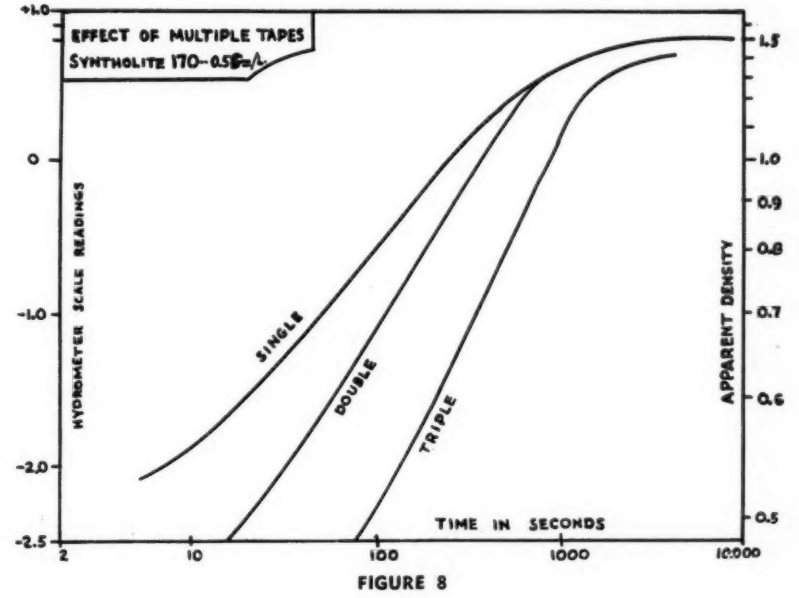


FIGURE 8

TABLE V

EFFECT OF PADDING TEMPERATURE ON REWETTING

Padding Temp, °C		25	50	70	25	50	70
		Seconds Rewetting					
		Tape Method			AATCC Method		
Wetting Agent	*Conc, g/l*						
Nekal NS	4	4	4	2	8	11	2
Chemsol 916	5	29	23	7	321	410	44
Deceresol OT 85	1.25	7	5	2.5	12	7	4
Syntholite 170	1	23	18	4.5	80	51	6
Amylnaphthalenesulfonate 40%	2.75	19	12	4	131	25	..
Igepol CA Extra High Conc	1	23	21.5	12	158	98	35
Sulfobulyloleate 40%	2.5	16	10.5	3	68	40	5
Chemsol 935	4.2	22	8.5	2	98	19	2.5
		Average of two tests, which check within 0.5 to 2 seconds.			Average of 4 to 6 tests of high variability.		

rapid surface spreading. Thus, for systems where capillary penetration is important, an optimum concentration of wetting agent must exist which is just enough to bring the contact angle below 90°.

After examination of the curves of Fig 8, we can see that we are not dealing with a simple relationship of volume of air to weight of cotton. We must take into consideration the form of the cotton (yarn number, twist and ply; fabric weave and density), the geometry of the sample (size, shape, and ply) and its disposition in the wetting solution (vertical or horizontal; depth of immersion). All these factors influence the rate at which air can be displaced from the cotton material.

Reutenauer (9) has noted that the discs sink in about half the time predicted from rate-of-wetting curves, and Table I of this paper shows that 1-inch squares (surface test) sink in about two-thirds the expected time. However, in another test, 1¼ x 9-inch tapes were floated on the surface and sinking-times were found to be about 15% *higher* than predicted from the curves.

II EXPERIMENTAL PART—REWETTING

The technique of running rewetting tests by the weighted tape method was described in the previous paper of this series (4). It has since been pointed out by Blumenstein (15) that the effect of *application* temperatures on the final rewetting speed of fabrics is very great and must be taken into account in any evaluation tests.

In this work the effect of padding temperature, time of immersion, time and temperature of drying, and temperature of rewetting medium were investigated for several commercial rewetting agents at several concentrations. The extent to which all these variables affect rewetting speeds makes it evident that proper evaluation of rewetting action is no simple matter.

The wetting agent was dissolved at 80°C. One-yard lengths of tape were immersed and padded 3 times, and the pickup was determined after each padding. The tapes were dried at room temperature and then in the oven at 100°C for 5 min. After 24 hours, 9-inch lengths of tape were tested with a 1-gram hook (in soft water at 25°C), and AATCC specular reflection tests were run on the same tape fabric.

The average pickup after each of 3 consecutive paddings (without intermediate drying):

1), 94%; 2), 86%; 3), 83%.

The decrease in pickup for 3 successive paddings is very definite. Although it might be expected that increased penetration should *increase* pickup, the dissolving out of soluble components in the cotton may account for the decrease.

TABLE VI

EFFECT OF NUMBER OF PADDINGS AND IMMERSION TIME ON REWETTING SPEED

A Chemsol 916		Seconds For Rewetting At 25°C							
Grams per Liter		5	5	5	5	2	2	2	2
Padding Temp °C		25	50	75	90	25	50	75	90
Seconds Immersion	*No. of Paddings*								
30	1X	66	69	37	9				
30	2X	38	48	18	9				
30	3X	42	44	14	7	127	186	32	16
30	4X	29	33	14	5	118	174	24	13
30	5X	34	29	11	4	103	103	19	8
60	1X	52	36	19	12				
120	1X	46	30	15	14				
240	1X	33	32	14	7				
480	1X	25	28	10	4				
960	1X	20	17	7	2				
B Amylnaphthalenesulfonate, 40%									
Grams per Liter		2.75	2.75	2.75	2.75	1	1	1	1
Padding Temp °C		25	50	75	90	25	50	75	90
Seconds Immersion	*No. of Paddings*								
30	1X	65	50	23	20				
30	2X	54	30	17	14				
30	3X	32.5	22.5	8.5	7.5	122	106	57	45
30	4X	26	18.5	5.5	10	112	81	43	33
30	5X	24	16	5	10	101	61	36	28
60	1X	62	42	21	18				
120	1X	50	34	19	15				
240	1X	42	33	10	11				
480	1X	34	29	6.5	8				
960	1X	30	20	5.5	7				
C Sulfobutyloleate, 40%									
Grams per Liter		2.5	2.5	2.5	2.5	1	1	1	1
Padding Temp °C		25	50	75	90	25	50	75	90
Seconds Immersion	*No. of Paddings*								
30	1X	70	53	26	16				
30	2X	58	37	20	10				
30	3X	40	30	11	7				
30	3X					89	61	32	12
30	4X					73	55	26	9
30	5X					54	48	15	6
60	1X	66	45	22	16				
120	1X	59	36	20	15				
240	1X	42	33	17	9				

TABLE VII

SUCCESSIVE PADDINGS THROUGH 500 ML OF 0.275% AMYL NAPHTHALENE SULFONATE (40%) AT 25°C

Strip No.	*Rewetting Tests* 1	2	*Avg*
1	32	29	30½
2	34	30	32
3	38	32	35
4	40	41	40½
5	36	34	35
6	40	35	37½
7	34	29	31½
8	33	29	31
9	36	36	36
10	34	35	35½

Definite progressive improvement in rewetting with increasing pad temperatures occurs by both test methods and with all the rewetting agents tested.

In the tests of Table V the tapes were padded three times to insure saturation. In Table VI is shown another series run with three commercial rewetting agents to determine the effect of number of paddings or time of immersion in the solution of wetting agent.

Table VI again confirms the vast improvement in rewetting obtained by increasing the padding temperature. However, it points out another serious variable, namely, *time* of *immersion* or number of dips and nips. The improvement in rewetting with longer immersion or more paddings is so spectacular that one is tempted to conclude that the wetting agent must exhaust onto the cotton. However, the fact that three widely differing chemical types of wetting agents, none of which is known to have substantive properties, all show the same effect renders this theory less likely. As an added check, ten one-yard strips of tape were successively immersed in the same 500-ml solution at 25°C for 60 seconds, squeezed through the padder, dried, conditioned and tested at 25°C (Table VIII).

Thus, there appears to be no evidence of progressive exhaustion of surface-active material from the liquor. A possible explanation for the improvement with both increasing temperature and time of impregnation is that some sort of scouring action takes place on the cotton. Removal of soluble material and, perhaps, emulsification of some oils or waxes may present a cleaner cotton surface for proper adsorption and orientation of rewetting agents.

EFFECT OF DRYING AND BAKING CONDITIONS——To determine the effect of drying and baking conditions, a series of tapes was padded at 25, 50, and 75°C, dried or baked as indicated in Table VIII, conditioned 24 hours and tested for rewetting at 25°C.

It is to be noted that the pickup decreases with increasing temperature (possibly because of a combination of the scouring effect on the yarn and the reduced viscosity of the solution at elevated temperature).

Best results were obtained for drying at 100°C for the 25 and 50°C paddings, but, for the 75°C paddings, air drying seemed better.

Baking at elevated temperature following air drying reduced the effectiveness of rewetting.

Since drying at 100°C is a better approximation to commercial practice, another series of tests was run to determine the effect of time of drying at this temperature (Table IX).

TABLE IX

EFFECT OF DRYING TIME AT 100°C

		Seconds Rewetting				
A	Amlynaphthalenesulfonate, 40% at 2.75 g per liter					
	Padding Temp, °C	*20*	*40*	*60*	*80*	*95*
	2) +5 min @ 100°C	34	22	15	6	5
	1) Barely Dry	42½	21½	16½	6½	6
	3) +10 min @ 100°C	30	20	15	5	4½
	4) +20 min @ 100°C	30	21	17	5	4½
B	Sulfobutyloleate, 40% at 2.5 g per liter					
	Padding Temp, °C	*20*	*40*	*60*	*80*	*95*
	1) Barely Dry	33	28½	12½	5½	3½
	2) +5 min @ 100°C	37	22	10½	4½	3
	3) +10 min @ 100°C	31½	22	11½	3½	2½
	4) +10 min @ 100°C	29	25	16	5½	3½
C	Chemsol 916 at 5 g per liter					
	Padding Temp, °C	*20*	*40*	*60*	*80*	*95*
	1) Barely Dry	44½	41	30	10	5½
	2) +5 min @ 100°C	39	46	31	11	7
	3) +10 min @ 100°C	39	40	32	8½	7
	4) +15 min @ 100°C	41	43	35	12½	6½

Thus, if the fabric is definitely dry and is baked a few minutes extra at 100°C, additional drying time seems to have no further effect. (In this series a padding temperature of 95°C was included, and it is interesting to note that there is, in general, very little improvement over the 80°C padding temperature).

As might be expected, rewetting speed is increased markedly by increasing the padding temperature.

EFFECT OF REWETTING TEMPERATURE——As might be anticipated, rewetting speed increases very markedly as the temperature of the water is increased.

While the above phenomenon in Table X is hardly unexpected, it may serve to call the attention of the finishers to the vast benefits obtainable by heating water for rewetting above 50°C.

TABLE VIII

EFFECT OF DRYING AND BAKING TEMPERATURE

	Amylnapthalene-sulfonate, 40% at 2.75 g/l			*Sulfobutyl-oleate, 40% at 2.5 g/l*		
Padding Temp, °C	25	50	75	25	50	75
Pickup, %	92	79	75	86	80½	75
1) Dried @ 100°C (abt 15 min)	24	22	6	26	11½	5
2) Air-dried @ 25°C	40	23	2½	38	15½	2
3) Air-dried, then baked 5 min @ 50°C	52	23	3	40	19	2½
4) Air-dried, then baked 5 min @ 75°C	74	36	8	51	20	4
5) Air-dried, then baked 5 min @ 100°C	66	38	8	55	26	7½

CONCLUSIONS

An improved hydrometer method has been adapted for rate-of-wetting tests on vertically extended tapes, and the resulting curves have been compared with standard weighted-tape tests and with unweighted-patch and unweighted-tape tests. The hydrometer method gives readily reproducible results if performed with care. Weighted- and unweighted-vertical-tape test results correspond quite well to the calculated points on the rate-of-wetting curves.

Crossovers in the rate-of-wetting curves for different concentrations do not occur for vertically extended single tapes. Occurrence of crossovers when skeins, folded samples, or doubled samples are employed is caused

TABLE X

EFFECT OF TEMPERATURE OF WATER USED IN REWETTING

	Padding Temp, °C	Rewetting Temp°C	Seconds for Rewetting 25	50	75	90
A	Chemsol 916 at 2 g/l	25	182	68	40	9
		50	120	40	37	1
		75	28	7	4	1.5
		90	22	7	2	..
B	Amylnaphthalenesulfonate, 40% at 1 g/l	25	76	42	45	26
		50	63	46	56	1
		75	46	33	63	1
		90	30	21	48	1
C	Sulfobutyloleate, 40% at 1 g/l	25	138	51	56	4
		50	78	44	52	18
		75	27	14	25	6
		90	19	11	24	1.5

by mechanical air entrapment in cases where capillary penetration is important. It is difficult to generalize on the significance of the phenomenon, and interpretation should depend on the individual technical application involved.

The mechanism of air displacement has been discussed, and tests indicate that the air travels in the void spaces in the fabric up to the top before being released. It was found that wetting speed is increased considerably by cutting the tape in segments to furnish more points at which air can be released.

The effect of various conditions on laboratory rewetting tests was determined. Increased padding temperatures up to about 80°C result in progressively better wetting. Increase in immersion time and number of immersions also improve rewetting. Since pickup is not improved by these conditions, and there is no evidence of exhaustion of the bath, it is suggested that partial cleaning of cotton surfaces may be responsible for these phenomena. Drying conditions were found to have some effect on rewetting results, and standardization of drying times and temperatures appear quite important. Rewetting efficiency is greatly improved by increasing the temperature of the water used in the rewetting step.

ACKNOWLEDGEMENT

The important contributions of Mrs Gertrude Lacoste to the experimental portion of this paper and the supporting work of Mrs Ruth Catterall are gratefully acknowledged.

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Calendar of Future Meetings

COUNCIL: Jan 18, April 18, June 13, Sept 19 (all in New York); Nov 6 (Boston).

GENERAL RESEARCH COMMITTEE: Dates and sites are the same as the Council's.

NATIONAL CONVENTIONS: 1952—November 6-8, Boston, Mass; 1953—Sept 17-19, Hotel Stevens, Chicago, Ill; 1954—Atlanta, Ga.

HUDSON-MOHAWK SECTION: Feb 1, Mar 21, May 2 (all at Jack's Restaurant); June 20 (Annual Outing).

MID-WEST SECTION: February 16 (Hotel Bismarck, Chicago, Ill); April 19 (Cincinnati, O); June 14 (Lake Lawn Lodge, Delavan, Wisc); October 4 (Hotel Bismarck, Chicago, Ill).

NEW YORK SECTION: Jan 11 (Hotel New Yorker); Feb 29 (Hotel McAlpin, New York); April 18 (Swiss Chalet); May 16 (Swiss Chalet); June 20 (Outing).

NORTHERN NEW ENGLAND SECTION: Jan 25 (Boston); Mar 7 (MIT); April 18 (LTI); May 16 (Andover Country Club); June 6 (Annual Outing, Merrimack Valley Country Club); Dec 6 (1952 Annual Meeting, LTI).

PACIFIC SOUTHWEST SECTION: Jan 11 (Nikabob Cafe, Los Angeles); March 28.

PHILADELPHIA SECTION: Jan 18 (Kugler's, Philadelphia); March 7 (Penn-Sheraton Hotel, Philadelphia); April 25 (Abraham Lincoln Hotel, Reading, Pa); June 13 (Outing, Lu Lu Temple Country Club, North Hills, Pa).

PIEDMONT SECTION: Feb 1-2 (Robt E Lee Hotel, Winston-Salem, N C; April 25-26 (Clemson House, Clemson, S C); June 6-7 (Ocean Forest Hotel, Myrtle Beach, S C); Sept 12-13 (Hotel Charlotte, Charlotte, N C).

Complexes——

(Concluded from Page P15)

At this point the white, unprinted portion of the goods will have a definite and unpleasant stain, but can be cleared by a modification of the customary soaping bath. To this bath, containing a mild detergent, are added small amounts of acetic acid and hydrogen peroxide, the strength and the temperature once again depending on the time of immersion of the goods. This final treatment produces prints of maximum fastness and whites of excellent clarity. No acetic acid or hydrogen peroxide need be used when the printing is done on dyed grounds.

A finishing treatment with a urea-formaldehyde or melamine resin will give even higher fastness ratings, and, in the case of overprints on dyed grounds, the resinous-copper complex may be added to the resin solution and applied on the pad. One decided advantage of this method is that no staining of the pad liquor occurs, and it is possible to change from heavy shades to pastels without loss of solution and with a consequent important saving in chemical costs.

In conclusion it is necessary to stress the fact that the investigational work on the processes outlined above is far from complete. Many more dyes remain to be tested and evaluated as to their suitability. Although satisfactory mill trials have been run, varying conditions will present new problems to be solved, and the solution of these problems will afford fresh information leading to even greater success in providing a new range of fast colors.

DISCUSSION

Question: Why do you use copper in the aftertreatment if, at the same time, you employ a chelating agent, which inactivates copper salts?

Answer: I think you misunderstand the application. The sequestering, or chelating agent is in the discharge paste and is therefore applied to the dyed goods only where the discharge paste falls and not over the whole goods. It thus does not remove copper from the undischarged portions of the pattern and does not impair the wash fastness of the colored ground.

Special Contribution——

A NEW METHOD OF DETERMINATION OF WETTING POWER*

G REUTENAUER, J P SISLEY AND MME S DUPIN
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INTRODUCTION

ONE of the most important properties of surface-active agents is wetting power. This accelerative effect of contact between a liquid and the solid which is immersed in it has found numerous practical applications *(1, 2)*. The preliminary and finishing treatments of textiles require the employment of surface-active compounds possessing high wetting power.

Many attempts have been made to relate the wetting power of a compound to its well-defined physical properties, which are scientifically measurable *(3)*. The phenomenon of wetting is closely connected with the surface tension and interfacial tension of solutions *(4)*. In the region where wetting is effected, there are found at the point of contact the liquid, air and the fatty or waxy compound fixed or deposited on the textile fiber; this compound resists wetting of the fiber *(5)*. Other factors enter into the reaction, but very little is yet known about them *(6)*.

In a previous paper *(7)*, we have shown, within certain limits, the correlation existing between the wetting power of a solution and its surface tension. These tests were made with the Dognon-Abribat tensiometer.

It should be possible to obtain more complete information regarding the factors active in wetting by use of apparatus better adapted for this purpose *(8)* or by a drop-counting method *(9)*.

However, practical methods should require the use of textile fibers. These are only applicable for the particular fabric used in the trials.

Studies have been carried out on portions of yarn to determine the degree of elimination of soil by a detergent solution. These trials are based on theory *(10, 11)*. Practical methods of measurement require the use of skeins of yarn of constant weight or samples of fabric of definite dimensions *(12)*. Methods utilizing the speed of penetration of surface-active solution into fabric are still very little used. Conventional methods are based on the sinking time of a sample of textile fibers when plunged into a solution of which the wetting power is to be determined. The sinking time is figured as that point at which the air occluded within the fibers is expelled sufficiently so that the apparent density of the fibers and the sinker is equal to the density of the solution. Such a principle of measurement is arbitrary and incomplete. As a matter of fact, in the case of cotton, sinking of the textile sample always involves the presence in the fiber of a considerable amount of air, even if no sinker is used. In many uses of surface-active agents, this phenomenon has no importance, but for other uses, particularly in the dyeing of fabrics in the greige, it is necessary to eliminate quickly the largest possible quantity of air.

On the other hand, in comparing two products at fixed concentrations, it is not certain that the activities of these products will be exactly the same from the start to the finish of the wetting. In other words, the curves of apparent density of fabric against time may be different for different products. It is necessary to study the paper of Edelstein and Draves *(13)* in order not to be surprised at the apparent contradictary results given by the various methods of determining wetting power, and, in addition, to avoid arriving at the conclusion that these methods have no practical value at all. As a particular example, in the Draves test *(14)*, if the weight of the sinker that holds the skein upright in the liquid is varied, sinking times are obtained, because of varying amounts of occluded air remaining in the sample, which vary with the weight of the sinker. If these figures are compared, without due interpretation, the results obtained may be abnormal and misleading.

It is interesting to use the Draves test for the study of the progressive elimination of air during the wetting of the fibers by a given wetting agent at a specified concentration. Shapiro has done this *(15)*. This worker takes as known the real density of the cotton fiber utilized and calculates, at various periods, the volume of air remaining within the cotton.

For practical reasons, Shapiro used pieces of tape in these tests in place of the skeins recommended in the official Draves test. The air occluded in the fabric before wetting is more constant, from sample to sample, than that contained in the skeins. An evaluation can be made on the basis of the proportion of air eliminated to the air initially occluded. Substitution of the tape for the skeins provides a close approximation of the conditions commonly observed in the popularly used Draves test, but reduces the number of discordant results obtained when the threads of the skeins are insufficiently separated from one another.

Use of the Draves test does not permit complete exploration of the wetting action of a product. As a matter of fact, by diminishing progressively the weight of the sinker attached to the fabric, the times required to eliminate larger and larger quantities of air can be measured. Even without sinker, the fabric, after sinking, still contains 20% of the initially occluded air. The author shows that the extrapolation of curves up to complete elimination of the air is not possible. In order to demonstrate this, he suspends a piece of tape from the arm of a hydrostatic balance and immersed in a surface-active solution and measures the variations in weight at various periods of time. In this way it is possible to adduce evidence of retardation in the rate of escape of air as total wetting approaches.

It is quite evident that this technique cannot be used in making control tests. The idea of Gruntfest, Hager and Walker *(16)* of using, for the determination of wetting

* Translated from the French by permission of the authors.

power, a sort of hydrometer to which a skein of threads can be attached, appears to be extremely attractive. These workers easily determine the escape of the air contained in the fibers in relation to the time. Before going very far into the study of various surface-active compounds with this hydrometric method, they were able to show that some surface-active agents give more complete wetting at very low concentrations than in solutions of high concentrations. These findings have been contradicted by Shapiro (loc cit) in his experiences with cotton fabric. He finds that it is better to determine wetting power by means of a tape than with skeins; the latter give results that are less reproducible. He finds that, in comparing different products, the wetting curves, plotted as sinking times, show a certain degree of parallelism. In other words, if two surface-active solutions show the same wetting power at the beginning of the wetting of the fabric, their several efficiencies are comparable still at the end of the wetting operation. This conclusion is likewise at variance with the trials of Edelstein and Draves (loc cit) conducted on cotton skeins.

METHOD OF DETERMINATION

We were interested in finding out the value of the information furnished by the apparatus suggested by Gruntfest. At the same time, we sought to compare these results with those obtained by the conventional wetting tests and to clear up, as far as possible, the contradictions existing between the various authors quoted above.

The hydrometer utilized (Fig 1a) was sent to us by J Valée who has used it for quite some time for control tests of wetting agents in his laboratory. It consists of a stem of Pyrex glass 1 cm in diameter suitably expanded into a bulb and surmounted by a calibrated glass tube having an external diameter of 0.5 cm.

The lower extremity of the stem terminates in a small reservoir carrying four glass lugs to which two skeins or two samples of fabric of equal weight can be attached parallel to the axis of the device. The upper part of the tube carries a graduated paper scale fixed on the interior. The apparatus is weighted by pouring a small amount of mercury into the lower section. The liquid to be tested is placed in a cylinder 6 cm in diameter and 60 cm high.

The quantity of mercury to be used and the maximum weight of cotton that the apparatus is capable of carrying must be calculated. When the device is loaded and immersed in the surface-active solution, part of the graduated stem should be above the surface of the liquid.

This hydrometer is very fragile on account of the glass lugs fused on to it. We have tried to simplify its construction as much as possible. A tube calibrated to a diameter of 0.6 cm and a length of 35 cm is blown out toward the center into a bulb with a diameter of 3 to 3.5 cm to serve as a float (Fig 1b). The lower extremity consists of a reservoir to hold the mercury; it is terminated by a small hook to which the cotton sample is attached. The sample is stretched by means of an anchor weighing about 3 to 4.5 grams. The weight of the anchor and the amount of mercury to be poured in have to be regulated in the same way as in the Gruntfest apparatus. With this modified form of apparatus, identical results were obtained for fabric samples as with the hydrometer previously described. With skeins, the threads are insufficiently stretched to keep them parallel, and the reproducibility of the tests is not as good.

No matter what type of hydrometer is used, it is necessary, first of all, to standardize the markings on the scale so as to be

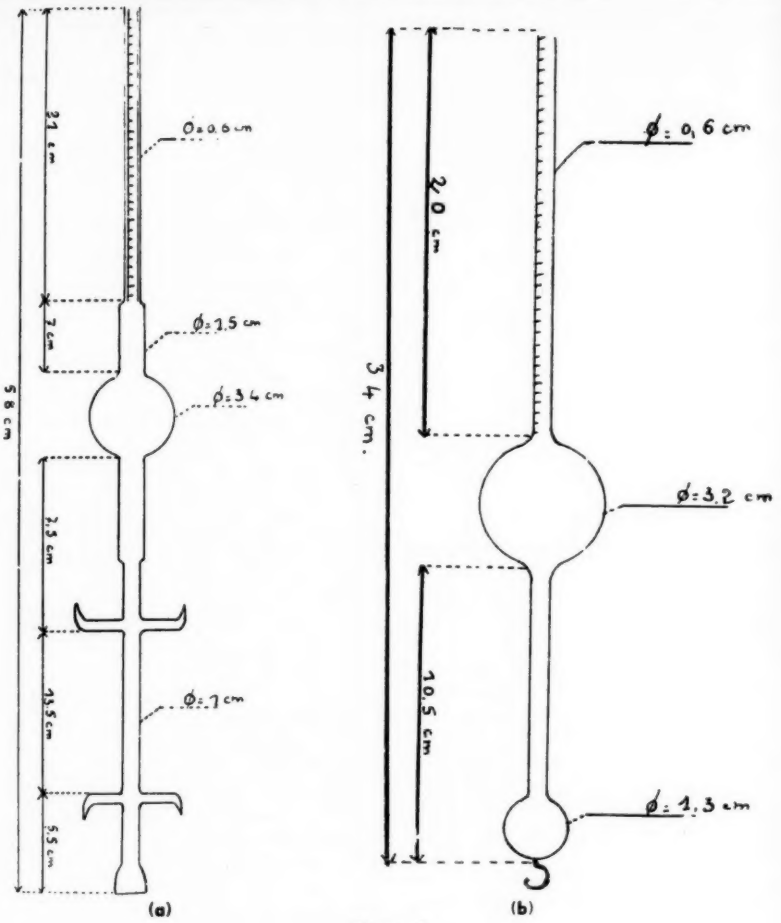


Figure 1

TABLE I

WETTING POWER FOR COTTON SKEINS

Products	Concentration %	Apparent Density: 1-min Wetting A	1-min Wetting B	10-min Wetting A	10-min Wetting B	1-hour Wetting A	1-hour Wetting B
Pot Laurate	0.02	0.30	0.33	0.35	0.41	0.41	0.46
	0.1	0.40	0.48	0.48	0.57	0.59	0.68
Sod Oleate	0.02		0.34		0.54		0.78
	0.1		0.72		1.00		1.11
Teepol	0.02	0.30	0.40	0.62	0.85	0.83	1.08
	0.1	0.92	0.98	1.19	1.13	1.24	1.18
Texaryl DS	0.02	0.43	0.63	0.81	0.93	0.97	1.15
	0.1	0.88	0.91	0.90	0.94	0.94	0.95
Cyclanon OA	0.02	0.35	0.35	0.77	0.70	0.96	1.00
	0.1	0.70	0.70	1.10	1.03	1.14	1.08
Marvepon NN	0.02		0.38		0.62		0.93
	0.1		0.95		1.08		1.10

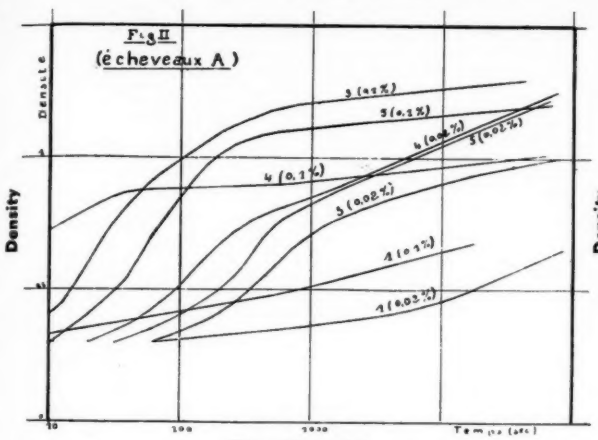


Figure 2

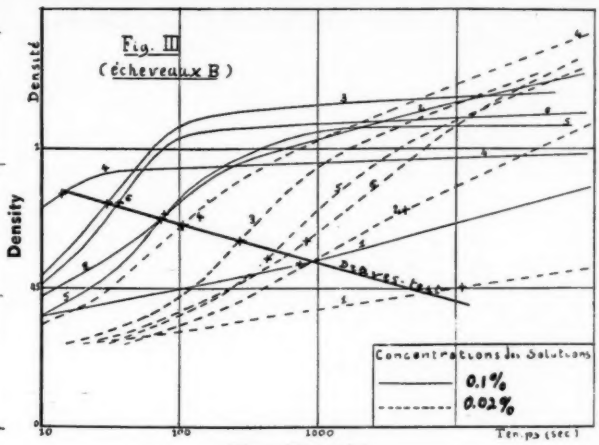


Figure 3

able to determine the volume of air expelled between two readings, or the apparant density of the fabric. The volume of air contained in the fabric is calculated from the following equation:

Vol of air = Pressure of the liquid on the cotton + the weight of the cotton − the volume of the cotton.

In the curves obtained with solutions of various wetting agents, it will be noted that, even after two days of contact, the density of the cotton depends on the wetting agent used. It is therefore impossible to know the real density of textile fibers and, consequently, volume of air retained by the fabric. We prefer to express the results as apparant density. Under these conditions, if a weight of 1 gram causes a sinking of the hydrometer of "p" graduations, and if "a_1" is the depression of the uncharged apparatus, depression of "a" graduations corresponds to an apparant density of

$$d_{ap} = \frac{2.5}{\frac{2.5 + a_1 - a}{p}}$$

the weight of fiber used being 2.5 grams in each trial.

EXPERIMENTAL RESULTS——The hydrometer was used in the study of the wetting power on cotton of the following agents:

(1) Potassium laurate (Characteristics of the lauric acid: iodine No., 2; acetyl No., 281; BP at 15 mm, 176°C; MP. 43°C.)
(2) Sodium oleate (Characteristics of the oleic acid; iodine No., 91; acetyl No., 196; BP 15 mm, 220°C; MP, 12°C.)
(3) Teepol, sulfonated secondary alcohol, 21% active.
(4) Texaryl DS, sodium dodecylbenzenesulfonate, 40% active.
(5) Cyclanon OA, sodium oleyl alcohol sulfonate, 30% active.
(6) Marvepon NN, sodium nonylnaphthalenesulfonate, 48% active.

These products were dissolved in distilled water at concentrations of 0.02 and 0.1%, figured on the content of active ingredient, at a constant temperature of 19°C.

The cotton used in the trials was either 2-ply raw yarn or cotton fabric having a count of 43 x 43 per sq cm.

Two skeins of 1.25 grams each were placed on the lugs of the hydrometer so as to be held in a vertical position. The length of the skeins was 11 cm.

The fabric was cut for each experiment into strips approximately 7.5 x 11.5 cm, each sample being adjusted to weigh 1.25 grams. These were attached to the lugs by means of threads. The weights of the fabric samples must be exact, as a variation of 0.1 gram entails an error of 2.5% in the density found.

The sinking of the hydrometer was recorded at various times from 10 seconds, after immersion, up to a period of 4 hours or 24 hours. The results are shown in curves, the abscissa carrying the logarithms of the times expressed in seconds and the ordinate the apparent densities of the cotton. On the same diagrams are also shown the sinking times for the various solutions, as obtained by the Draves test or the disc method.

As noted by Shapiro, the reproducibility of results is a little better when fabric is used in place of skeins. In all cases, the precision of the determinations, under conditions of constant temperature, is superior to that obtained by other methods of determination of wetting power commonly used.

Comparative trials were made with cotton of the same type but from stocks of different origin. Table I shows the apparent densities of both these types for wetting times of 1 minute, 10 minutes and 1 hour.

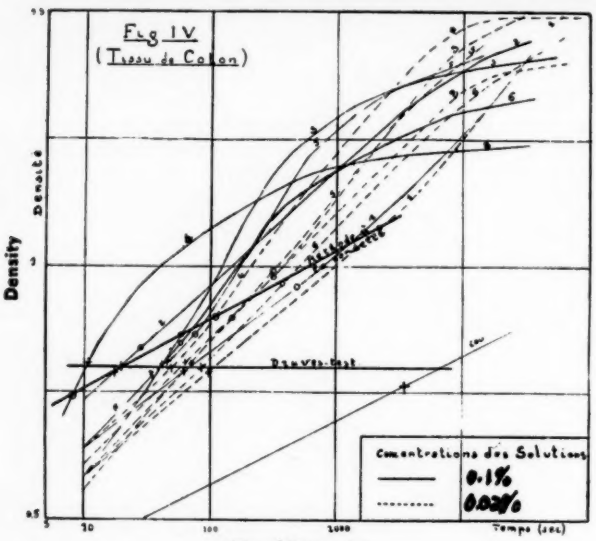
In Figure 3 the solid lines show curves given by concentrations of 0.1%, while the dotted-line curves represent results obtained from concentrations of 0.02% of the various products.

The graphs show clearly the similarity of results obtained with the two kinds of yarn, especially if the various solutions studied are compared with one another. Upon comparison of equal wetting times, the same

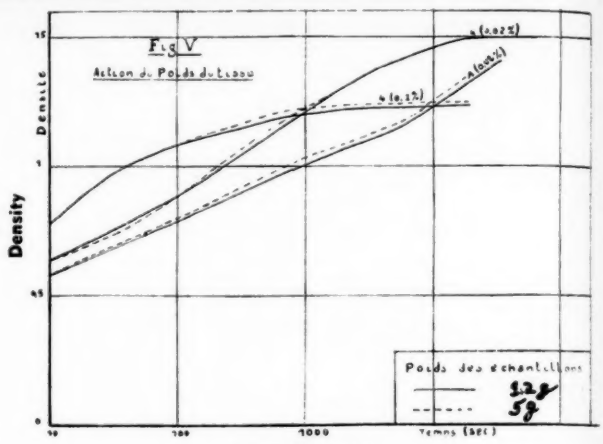
TABLE II

WETTING POWER FOR COTTON FABRIC

Products	Concentration %	Apparent Density 1-minute Wetting	10-minute Wetting	1-hour Wetting
Pot laureate	0.02	0.75	0.96	1.12
	0.1	0.78	0.98	1.14
Sod oleate	0.02	0.80	1.05	1.25
	0.1	0.91	1.14	1.32
Teepol	0.02	0.79	1.06	1.31
	0.1	0.87	1.25	1.36
Texaryl DS	0.02	0.82	1.15	1.38
	0.1	1.04	1.18	1.22
Cyclanon OA	0.02	0.79	1.07	1.30
	0.1	0.83	1.22	1.37
Marvepon NN	0.02	0.76	1.02	1.22
	0.1	0.85	1.16	1.26



Time (Seconds)
Figure 4



Time (Seconds)
Figure 5

classification of the products is obtained in both cases. Moreover, the differences in the figures exceed the possibility of experimental error. It is seen, therefore, that it is necessary to use yarn samples of the same origin in order to compare various products with exactness. The use of the hydrometer has clearly proved this point.

The wetting power of the same products was studied with the hydrometer in the same way, but with strips of cotton fabric in place of cotton skeins (Fig 4). The apparent densities of the fabrics, after 1 minute, 10 minutes and 1 hour, are shown in Table II.

Comparison of Figures 3 and 4 show that the differences in action of the various detergent solutions are more pronounced when skeins are used than when woven fabrics are used. This is seen very clearly in Table III, in which wetting powers are expressed in direct comparison with that of the least active (0.2% potassium laurate), which is considered as 1.

With the use of larger samples of fabric, it was hoped to arrive at greater precision on account of the greater displacement of the hydrometer. Fig 5 shows the results obtained by using samples of 1.2 grams and 5 grams. Variation of weight of sample of fabric has no influence on the measurement of wetting power. Moreover, the precision of the method is not sensibly improved by increasing the weight of the cotton fabric.

Upon comparison of the behavior of the curves representing the wetting of the skeins with that of the curves obtained with the fabric, it seems that, in the case of the latter, the curves are more nearly parallel with one another, particularly in the weaker concentrations. Hence, we understand the divergence in the conclusions of Shapiro and Edelstein in their respective researches; the first contends that there is a constant relation, as between the various wetting agents, during the entire wetting time, while the second maintains, as we have also found here, that the wetting curves, as a function of time, very often cross one another. In reality, if it is sought to classify various solutions according to their wetting power, it is found that often a wetting agent which is more active than another at the beginning of wetting shows less wetting effect when the time of contact of the cotton with the solution is prolonged, even in the case of fabric.

Table III makes it possible to classify the various surface-active solutions according to their wetting actions after the times noted. It is apparent that this classification is substantially the same, no matter whether the samples are in the skein form or in the form of woven fabric. The divergences observed in the use of these two methods are probably due to the different origin of the cotton in the skeins or woven samples, respectively, rather than to the form of the samples. Therefore it would seem to be better, in most cases, to use the cotton in skein form rather than in the form of fabric.

COMPARISON OF THE HYDROMETER METHOD WITH CONVENTIONAL METHODS——The wetting power of the solutions studied by the hydrometer method, as described above, was determined by three methods commonly used in industry:

(1) Draves test with a 5-gram cotton skein weighted with a hook weighing 1.5 grams.

(2) Draves test with a strip of cotton fabric weighing 1.85 grams measuring 22.8 cm in length by 6.4 cm in width, with a hook weighing 0.5 grams. (As far as possible, we followed the same conditions as those of Shapiro).

(3) The fabric disc test plunged into the liquid in the horizontal plane by means of a funnel.

The same yarn and the same fabric were

TABLE III

COMPARISON OF WETTING POWER

Product	Concentration %	Apparent Density: 1-min Wetting, Yarn B	1-min Wetting, Fabric	10-min Wetting, Yarn B	10-min Wetting, Fabric	1-hour Wetting, Yarn B	1-hour Wetting, Fabric
Pot laurate	0.02	1	1	1	1	1	1
	0.1	1.45	1.04	1.39	1.02	1.47	1.02
Sod oleate	0.02	1.03	1.06	1.32	1.10	1.70	1.12
	0.1	2.18	1.21	2.44	1.19	2.42	1.18
Teepol	0.02	1.21	1.05	2.07	1.11	2.35	1.17
	0.1	2.97	1.16	2.76	1.30	2.57	1.22
Texaryl DS	0.02	1.91	1.09	2.39	1.20	2.50	1.23
	0.1	2.76	1.39	2.29	1.23	2.07	1.09
Cyclanon OA	0.02	1.06	1.05	1.71	1.12	2.18	1.16
	0.1	2.12	1.10	2.51	1.27	2.35	1.22
Marvepon NN	0.02	1.15	1.01	1.51	1.07	2.02	1.09
	0.1	2.88	1.13	2.63	1.21	2.39	1.13

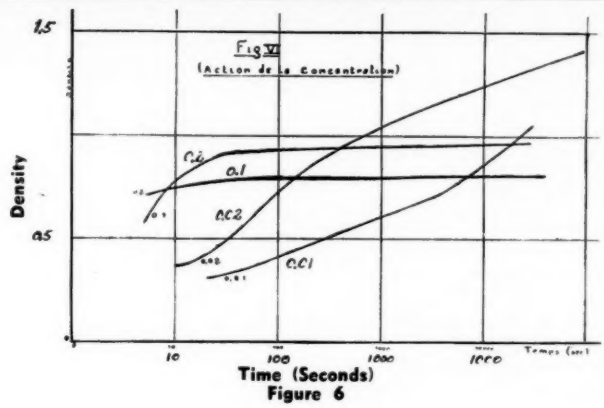
used in these tests. In the graphs in Figures 3 and 4 the results thus obtained are recorded for each wetting solution showing the wetting times (Draves tests are marked with a cross and disc tests with a circle). These points fall approximately in a straight line; for the purpose of classifying these agents, there is good agreement between the different methods, both for skein and fabric.

In principle, the sinking of the cotton, in each of these types of tests, should produce the same apparent density of the fiber: 0.82 for the Draves test with skein, 0.80 for the Draves test with fabric and 1 for the method using the unweighted disc of fabric. The second method alone gives figures agreeing with those obtained by the hydrometer method.

In the Draves test with skein, sinking is much more rapid when the wetting power is lower. It is easy to account for the lack of agreement of the results obtained in the Draves test and the hydrometer tests: it is due to the fact that the skeins are cut in the former but not in the latter.

The hydrometer test was also made with cut skeins, with which the speed of wetting was greatly increased. If the strands of the yarn are well separated, the results obtained by the hydrometer and by the Draves test agree exactly. It may be remarked that the cutting of the skeins changes all the curves according to a very definite law, and this does not involve any variation at all in the determination of the relative activity of the different solutions.

The differences observed as between the disc method and the hydrometer method with the use of a fabric sample are more difficult to explain. The difference is even greater as the wetting power increases, and the sinking times of the disc, generally speaking, are shorter than would be shown by the curves obtained by use of the hydrometer. The disproportion of the surface area of the samples of fabric used in each of these tests cannot be responsible, as we have indicated previously, since the size of the fabric does not make any difference in the results obtained with the hydrometer. The two tests utilizing the strips of fabric in the vertical plane (Draves test and hydrometer) give concordant results. It must be that the disc registers higher wetting power because the fabric is tested in the horizontal plane. When the fabric is held in a vertical position, minute bubbles of air remain imprisoned in equilibrium in the vertical meshes of the fabric, even when the fibers are thoroughly wet. In a similar manner, it may be possible to explain the anomalies observed by Gruntfest, Shapiro and ourselves when the concentration of the solution of certain surface-active compounds is varied.



Time (Seconds)
Figure 6

EFFECT OF CONCENTRATION OF SURFACE ACTIVE COMPOUND——It seems logical to suppose that increase of surface-active agent in a solution would result in an increase in wetting power. In other words, for the same wetting agent and for the same wetting time, the apparent density of the cotton should be higher in proportion as the concentration of the solution is increased. Although this is so for sufficiently short wetting times, it happens that the curves of apparent density cross one another. After a certain time, a product seems to be less active in higher concentrations. This is in accordance with the experiences of Gruntfest and Shapiro, working with skeins. When cotton fabric is used, the same conclusion is reached, providing the tests are prolonged for a sufficient period of time.

This phenomenon seems to follow a general rule, as shown in Figure 3. In fact, if the wetting power of a solution is high at the start of the wetting, its curve rapidly reaches a level, whereas, in the case of solutions having low content of wetting agent, the apparent density of the fabric increases gradually up to the point of almost complete elimination of air.

The effect of concentrations on wetting power, as measured by the hydrometer, was made the subject of a special study with Texaryl, a product which exhibits this phenomenon of the crossing of the curves very distinctly. Preliminary tests were made to make sure that the presence of impurities, such as mineral salts and unsulfonated fractions in the commercial product, would not interfere with the wetting power. Table IV and Figure 6 give a resumé of the results obtained with concentrations of 0.01 to 0.2% of this product. Cotton skeins were used.

TABLE IV

EFFECT OF VARYING CONCENTRATIONS

Concentration %	Apparent Density 5-sec wetting	10-sec wetting	1-min wetting	10-min wetting	4-hour wetting
0.01 ..			0.37	0.56	0.93
0.02 ..		0.37	0.63	0.98	1.27
0.1 ..	0.58	0.78	0.91	0.94	0.96
0.2 ..	0.61	0.74	0.79	0.79	0.80

For wetting times of less than 10 seconds, the wetting power, as determined by means of the hydrometer, increases regularly with increase of concentration of the solution. But at sufficiently long wetting times, the curves cross one another, so the determination of the apparent density of the skein would seem to show less wetting activity on the part of Texaryl in higher concentrations than in low concentrations.

It does not seem possible to explain this anomaly on the basis of the formation of micelles, since, for this group of products, this phenomenon is connected, not with the concentration, but solely with the wetting power at zero time. It seems possible that a secondary phenomenon, particularly when the surface activity of the solution is high, may enter into the wetting action and retard the escape of air from among the mass of fibers. We venture to offer the following hypothesis based on the observation of the formation of air bubbles during wetting. If the solution possesses only weak wetting power, the air travels along the length of the fibers from which it is detached in the form of large bubbles. On the other hand, if the solution has strong wetting power, the air is separated immediately from the cotton and it is possible that part of the air remains in the form of much smaller bubbles when the surface tension of the solution is lower. These bubbles are retained physically by the already wetted fibers. This air does not hinder in any way contact of the cotton and the liquid, and, as Shapiro has stated, the greater part of it is eliminated by agitation.

However, the importance of this phenomenon from the practical point of view should not be exaggerated, since this crossing of the curves, in most cases, only occurs in wetting times of about 10 minutes in work with solutions of the concentrations

usually employed of 1 gram per liter, calculated on the active ingredient, or less.

SUMMARY AND CONCLUSIONS

A study has been made of a new way of determining wetting power, known as the hydrometer method. It can be effectively carried out with either cotton skeins or strips of cotton fabric. The results thus obtained accord well with those given by other wetting-test procedures. The precision of the hydrometer is superior to that of oth r methods. The results are expressed in a more scientific manner and are in direct proportion to the elimination of air from the fiber.

The principal feature of this procedure is that it makes it possible to observe the operation of wetting as a function of time. In this way, a fundamental study of the action of surface-active agents on textile fibers is possible. In particular, the hydrometer method brings to light certain anomalies which show the limit of exactitude realizable by a procedure making use, in one way or another, of the apparent density of a textile fiber or fabric.

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Ether Linkage——

(Concluded from Page P14)

in strong sodium-hydroxide solution to be effective when applied like the dyes. Some reaction was obtained when water solutions of the compounds were applied to the fabric, dried on, and then 20-percent sodium hydroxide applied and the fabrics cured. However, when the resulting fabrics were diazotized and developed with various phenolic substances, the depth of color was much less than obtained by etherifying the dyes themselves with the fabric.

FASTNESS TO WASHING AND TO LIGHT——Fabrics colored by etherifying dyes to the cellulose by the method described in this paper had outstanding (Class 5) washfastness when tested by AATCC Standard Method 36-45 No. 4. They also showed little loss of color when boiled in 1-percent sodium-hydroxide solution for 6 hours. Their lightfastness was only fair. In Fade-Ometer tests (AATCC Tentative Test Method 16-45) some were better than the No. 3 standard and others slightly worse, all showing detectable fading in 20 hours. In direct comparison with cotton fabric dyed with commercial developed azo colors they showed nearly equal lightfastness and much better washfastness.

ACKNOWLEDGMENT

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(6) Ward, K, Jr, *J Am Chem Soc* 57, 914 (1935).

DISCUSSION

Question: Was the fire or mildew resistance of the cotton increased by your dyeing method?

Answer: The fire resistance as simply determined with a match was not improved; mildew resistance was not measured because we expected no improvement. We are interested in flameproofing with dye, but believe that there would have to be a lot more dye on the fiber than obtained by this method before a fire-retardant effect would be observed. One of the difficulties of the method is that the reaction is sluggish and deep shades are not obtained.

Q: Can you say anything about the economies of dyeing by your method for a given depth of shade?

A: No, not in this preliminary study. As a matter of fact, the action of combination is so sluggish and such a small proportion of the dye combines as we conducted the reaction that the process is not at all commercial. We need a catalyst or some way to speed up combination at a lower temperature. One advantage is that mercerization takes place at the same time as dyeing.

Q: How strong is the caustic soda solution?

A: Twenty percent by weight. Above 20% the dye solubility was found to drop off too much.

Q: Does this dyeing process work any better on regenerated cellulose?

A: We have not tried viscose rayon.

Q: Have you tried the reaction of 2-para-aminophenoxyethylsulfuric acid itself with treated fabric?

A: Yes, and, though we knew we had some reaction, this chemical is so insoluble in mercerizing caustic soda that we could not get much to react. The dyes are more soluble in caustic soda than the intermediate. We thought of introducing solubilizing groups into 2-para-aminophenoxyethylsulfuric acid, such as hydroxy groups, but the chemistry was too difficult for us. Even on paper the introduction of hydroxy groups involves a three- or four-step process.

Q: Do you intend to work further?

A: No. Flameproofing is a more pressing problem.

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1952 Committee Chairmen—Philadelphia Section

EDWARD C DIEHL, Chairman, Philadelphia Section, has appointed the following Committee Chairmen for 1952:

Intersectional Contest——M J Reider, G W Bollman & Co; *Program*——T H Hart, Hart Products Corp; *Dining*——F E Nevins, Ciba Co, Inc; *Membership*——M A Noonan, Becco Sales Corp; *Outing*——J L Fancourt, W F Fancourt & Co; *Bylaws*——P Theel, Philadelphia Textile Institute; *Publicity*——J W MacNeill, American Aniline Products, Inc; *Corporate Membership*——C T Anderson, Ciba Co, Inc; *Sectional Research*——V T Hartquist, Jeffries Dyeing Wks; *Olney Award*——E C Bertolet, Temple University Research Institute.

EMPLOYMENT REGISTER

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Abstracts

(Continued from Page 12)

Achieving Alkali Penetration in the Mercerization of Cotton Piece-goods

Anon, *Textile Recorder* 69, 88-90, September, 1951.

In the mercerization of cotton fabrics it is of the greatest importance, if the fabrics are to acquire maximum luster increase and be capable subsequently of being evenly dyed, that the caustic soda solution used should be brought into contact with every fiber.

It is usual in the mercerizing process to employ a cold solution of caustic coda of about 50° Tw. Such a liquor contains about 22.5 per cent NaOH and, being of considerable viscosity, does not readily penetrate cotton materials, particularly if these are made with tightly twisted yarns. Consequently, means have to be adopted to assist penetration.

Perhaps even more important than penetration is the sometimes overlooked requirement that a sufficient volume of mercerizing liquor should surround each fiber for at least one-half to one minute. During processing, each fiber is induced by the alkali to change its original twisted ribbon-like form and to become cylindrical or rod-like in character, and it is in this change that it absorbs water and chemically combines with the caustic soda.

It should be pointed out that cotton fabrics as delivered to the finisher invariably contain many impurities, not only those commonly found in raw cotton but those which are added during conversion of the raw cotton into yarn and fabric. It is an advantage to rid cotton fabrics of these various impurities before mercerization, particularly those which reduce the absorbency.

It should be borne in mind, however, that much of the success of mercerization is due to the fact that each cotton fiber possesses a cuticle which acts as a kind of semipermeable membrane between the cellulose inside the cuticle and the mercerizing liquor outside. This cuticle also plays an important part in controlling and ensuring even swelling of the cellulose so that each fiber may ultimately acquire a cylindrical form. It is important, therefore, that any preparatory treatment should not weaken or destroy this cuticle, as may be the case if the fabrics are over-purified.

There still remains the possibility of assisting the mercerizing process by the use of mechanical and chemical aids. As to the latter, there is no doubt that the use of suitable wetting agents does assist penetration in mercerization, and that by their use more evenly mercerized fabrics can be obtained. The earliest wetting agents used for this purpose were based on phenol and cresol. Quite a considerable amount of research has been carried out in this field, and many wetting agents are now available which are free from cresol.

As mechanical aids, the author recommends the use of two padding mangles, each equipped with three bowls, and the installation in each mangle of a "suction slot", submerged in the mercerizing liquor, over which the fabric passes while a pump draws the liquor continuously through the fabric into the slot. He states that penetration is considerably increased by this device.—WHC

Rayon and Synthetic Fibers: Antishrink Finishes

Anon, *Dyer* 106, 395, 397, September 21, 1951.

There are strong indications that antishrink finishes will be more generally applied not only to a variety of types of fabrics but to a much larger number. Some of the finishes, fundamentally, may be modified anticrease processes, and as such may offer only the same problems to the dyer. These will not be as effective as the straight antishrink processes in that they will possess only a limited degree of fastness to washing, and will have the further defect of initially increasing the weight of the fabric to an appreciable extent.

The straight antishrink processes will be based mainly on the use of an aldehyde glyoxal, either formaldehyde or a dialdehyde. Such processes depend on cross bonding of the cellulose molecules, and involve the use of acid catalysts. The increase in weight of the treated fabric is not significant, but the concentration of the effective chemicals used is greater than in the anticrease process, and the effect on susceptible dyes is greater. This involves more rigid selection of both direct and acetate dyes. Vat dyes are in the main unaffected, as are some azoics.

The antishrink processes in themselves are the same as the anticrease processes in that they involve the same mechanical treatment: padding, drying to the required dimensions, curing, washing-off, and final finishing. The washing-off is of considerable importance to the dyer; if inadequate, it may not only lead to the development of unpleasant odors, but may also have an unfortunate effect on the shade, particularly on exposure to sunlight.

Generally speaking, direct dyes will become faster to washing, and selected direct dyes faster to light also. The light fastness of other direct dyes may be unaffected or reduced to some extent.

A further consideration which affects the dyer is that of the ultimate tensile properties of the treated fabric. The application of an antishrink finish under well controlled conditions will leave the dry tensile strength of the fabric substantially unaffected, and the wet tensile strength will be increased. The dry extensibility will be slightly reduced, and the wet extensibility will be appreciably decreased.

The antishrink processes have been developed mainly for fabrics made from or containing viscose. Full treatment usually causes tendering of cotton. Acetate may be present in the fabric, although in shrink properties it will not be improved. —WHC

Engineering of Wear Resistant Fabrics

R G Stoll, *Papers AATT* 6, 71-4, June, 1951.

The improvement of the wear resistance of civilian, industrial and military fabrics is one of the most economical ways of conserving raw materials, production capacity and manpower, all of which are critical in times of national emergency.

Since 1942 the Quartermaster Corps has conducted field and accelerated field tests for determining the wear life of uniforms. A special proving ground, the "Combat Course" at Fort Lee, Va, was established by the Quartermaster Board for the evaluation of military textiles.

Combat Course tests of fatigue uniforms have shown that a warp sateen of a certain balance in yarn count and texture, worn with the filling side out, may be constructed to have up to 100 per cent more wear resistance than Army herringbone twill. Almost a threefold increase in wear resistance over the herringbone twill can be expected by the admixture of 25 to 50 per cent nylon staple in the filling yarns, which in this wear-resistant sateen construction protect the stress-bearing warp yarns.

The mechanism of breakdown in fabrics is substantially the same regardless of fiber type, yarn and fabric construction, finish and end use. This has been indicated by exhaustive microscopical examination by Clegg in England of hundreds of worn textile items, and also by our own comprehensive correlation studies of a large number of fabrics subjected to normal service wear, accelerated Combat Course wear and laboratory wear. These investigations showed that primarily bending and flexing stresses cause a transverse cracking of individual fibers, which gradually leads to the formation of holes at places of concentrated wear, or to the production of tears and splits in places where partial fiber breakdown has weakened the yarns, making them susceptible to tearing and snagging forces.

Tensile stresses or surface attrition on fabrics do not appear to be major wear factors. Consequently breaking strength and elongation as well as resistance to surface abrasion have been found to be

unreliable parameters for the characterization of the wear resistance of fabrics varying in fiber quality, yarn construction, texture or weave.

After numerous attempts, an adequate method was found for the laboratory evaluation of the resistance of yarns and fabrics to complex mechanical wear. This method essentially consists of a flex abrasion test in which yarn or fabric specimens are gradually disintegrated by bending and abrading around a thin bar under precisely controlled conditions.

Resistance to surface attrition and tear strength appear to be factors which should also be considered in predicting wear resistance, but with a lower relative importance than the flex abrasion results.

To carry out these laboratory wear tests under precisely controlled conditions, an instrument has been developed which is capable of measuring quantitatively resistance to flex abrasion, surface attrition and edge abrasion, each under dry and wet conditions.

The author shows the correlation which has been found to exist between the results of these laboratory tests and the Combat Course wear score.—WHC

Synthetic Fur for Cold Weather Clothing

J E Walker, *Papers AATT* 6, 108-10, June, 1951.

At very low temperatures such as are encountered in the Arctic and Antarctic regions and at higher altitudes, protection of the human being must be complete. When —40° F is ordinary and —60° F not unusual, no part of the human body can endure more than very short exposure to the elements without serious consequences.

The Armed Forces have generally adopted a parka type head covering trimmed around the face opening with long-haired fur which can be pulled in to form a partial barrier in front of the face. An evident and unavoidable result of this type of protection is frost and ice formation on the fur. This decreases and ultimately defeats the function of the fur ruff with loss of efficiency and potential hazard to the wearer. Therefore, a fur to give the best performance as a parka ruff must retard frost and ice formation and must be capable of being readily brushed free of the frost and ice that does form.

Wolverine fur has been found the best for this purpose, but wolf fur, being more available, has been more or less standardized by the Armed Forces.

The individual branches of the Service have been conducting investigations to develop noncritical substitutes for this type of material. The Army and Navy have tested various domestic furs, but the Air Force, after careful study, decided that the only real assurance of adequate availability lay in the development of a completely synthetic substitute for wolverine and wolf furs which would be free of strategic limitations.

From the psychological standpoint, the synthetic fur must be pleasing and, if possible, natural in feel and appearance; physiologically, the fur must be inert, nontoxic, nonirritating and odorless; functionally, the fur must form an effective partial barrier and maintain that effectiveness under and after all normal conditions of service.

It was decided to prosecute concurrent research endeavors with a knitted pile fabric manufacturer and with a woven pile fabric manufacturer in order to utilize the full ingenuity of the textile industry and to maintain a favorable competitive procurement situation on the developed product.

The knitting company succeeded in producing a nylon pile synthetic fur possessing the bulk of the attributes described in the research requirements. Cold chamber tests of this synthetic fur have yielded favorable results and cold weather service tests being conducted in Alaska and Canada, while not yet complete, are favorably indicative.

As a consequence, the nylon pile synthetic fur is being groomed for early standardization as a substitute, and probably as a replacement, for natural wolf and wolverine furs in cold weather clothing.—WHC

Notes on Silk Dyeing. Parts VI and VII. Weighting.

A G Tyler, *Brit Rayon & Silk J* 28, No 327, 60-1; No 328, 57-8, August and September, 1951.

Although most silk is dyed in the pure state, a certain quantity is weighted as well. The weighting of silk was probably first performed to replace the loss of weight occasioned by the removal of the silk gum, usually of the order of 25 per cent of the raw silk. If the weighting is carried further than this, it is found that the silk becomes swollen and so gives greater "cover" than the unweighted fiber. Besides the extra cover obtained, the handle of weighted silk differs from that of pure silk and is to be preferred for certain purposes; the draping qualities are also held to be improved.

The type of weighting employed determines whether this is to be carried out concurrently with the dyeing, or is to be an altogether separate process. As an example, if a purely mineral weighting is used, the use of tin phosphate and silicate baths is involved, which results in the formation of an extremely complex phospho-silicate of tin in the fiber. It is necessary to carry this out as an entirely separate process from the dyeing. Silk, after such weighting, has a similar appearance to that of the silk before weighting, except that the filaments are now swollen, the amount of swelling depending on the degree to which the fiber has been weighted. On the other hand, if the weighting involves the use of tannin bodies, with or without the addition of metallic salts, it is often difficult to say where the weighting ends and the dyeing begins, because all tannins are brown in color, some being very highly colored. If tannins are used in conjunction with iron salts, an almost black iron tannate is formed, which renders impossible the use of this combination for anything but black dyeing.

Tin-weighted silk may be dyed by some members of most classes of dyestuff, those of the acid, basic, direct, and vat classes being in regular use for this class of work. However, the fact that any particular dyestuff will dye pure silk well is no criterion of its behavior towards weighted silk.

Yarn is usually dyed with basic or acid dyes in a broken boiled-off liquor bath. Fabrics which are to be used for dress goods requiring the maximum draping qualities are, as far as possible, dyed in a neutral bath, while if they are required for tie fabrics they are dyed from an acetic acid bath. This is because a scroop finish is required for tie fabrics. Direct dyes which can be diazotized and developed are used for shades where good fastness to washing is required.

Vat dyes may not be dyed on weighted silk because of the alkaline nature of the dye-baths employed. They may be dyed, however, on the unweighted silk after which the dyed silk is weighted to the required degree. The vat leuco esters, on the contrary, may be used on weighted silk for light shades.

The main vegetable extracts used for weighting silk may be classified under the headings of tannins and logwood. Various tannins may be used, but that most commonly employed is sumach, the boiled-off silk being treated in a decoction of this tannin, which is readily absorbed by the fiber.

Silk weighted with sumach assumes a brown hue, so that it is difficult to dye shades other than dark browns or greys. The acid milling colors are usually employed, being applied from a neutral or slightly acid bath.

Mixed vegetable and mineral weightings are used in the dyeing of blacks. The silk is first mordanted with ferrous sulfate, and then dyed with a large quantity of oxidized logwood (or, "nitrate of iron" may be used, followed by a treatment with a tannin, to produce tannate of iron on the silk, which is then dyed with logwood).

Many variations in the methods used in producing black-weighted silks are described by the author.—WHC

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